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A SHORT
PHARMACEUTIC CHEMISTRY
INORGANIC AND ORGANIC

PHARMACEUTIC CHEMISTRY

STANISLAUS

P. H. RAVENHILL & SONS, LTD.
LONDON

A SHORT
PHARMACEUTIC CHEMISTRY
INORGANIC AND ORGANIC

BY

I. V. STANLEY STANISLAUS, M. S., PHAR. D.,

*Professor of Pharmacy and Organic Chemistry and
Dean of the School of Pharmacy of the Medico-
Chirurgical College of Philadelphia*

AND

CHARLES H. KIMBERLY, B. S., (in Pharmacy) PH. D.,

*Professor of Applied Chemistry in the School of
Pharmaceutic Chemistry of the Medico-
Chirurgical College of Philadelphia*



SECOND EDITION

PHILADELPHIA
P. BLAKISTON'S SON & COMPANY
1012 WALNUT STREET

1908

RS421
S8
GENERAL

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Printed by
The Maple Press
York, Pa

ERRATA.

- Page 20.—Under **OXYGEN** read—"A gaseous element.
Symbol O. Atomic Weight 16. Valence 2."
- " 69.—Line 11: "1.52" should be "1.403".
- " 69.—Line 12: "86° C." should be "120.5° C."
- " 69.—Line 25: Omit "H—HCN".
- " 73.—Line 3: "1.83" should be "1.826."
- " 74.—Line 7: "AsO₃" should be "As₂O₃".
- " 74.—Line 22: "1.71 at 15° C." should be "1.707
at 25° C."
- " 75.—Line 2: "At 15° C." should be "at 25° C."
- " 87.—Line 14: "Argenti nitras dilutus" should be
"argenti nitras mitigatus."
- " 113.—Line 10: "Ferri sulfas" should be "ferri
sulphas."
- " 113.—Line 18: "Ferri sulfas exsiccatus" should be
"ferri sulphas exsiccatus."
- " 113.—Line 22: "Ferri sulfas granulatus" should be
"ferri sulphas granulatus."
- " 114.—Line 21: "37.8%" should be "29%".
- " 114.—Line 22: "62.9%" should be "42.8%".
- " 137.—Line 26: "60%" should be "55%".
- " 178.—Line 8: "198.3" should be "198.5".
- " 178.—Line 14: "198.3" should be "198.5".
- " 223.—Line 13: "40° to 70° C." should be "45°
to 60° C."
- " 223.—Line 20: "80° C." should be "57.2° C."
- " 317.—Line 8: "34.6° C." should be "35.5° C."
- " 343.—Line 13: "500 parts" should be "360 parts."
- " 437.—Line 3: "115° C." should be "113° C."
- " 547.—Line 18: "170° to 185° C." should be "155°
to 165° C."

TABLE

THE following table gives a summary of the results of the experiments conducted during the year 1881, and is intended to show the effect of the various factors on the growth of the plants. The table is divided into two parts, the first giving the results of the experiments on the growth of the plants in the open air, and the second giving the results of the experiments on the growth of the plants in the greenhouse. The first part of the table is divided into two columns, the first column giving the results of the experiments on the growth of the plants in the open air, and the second column giving the results of the experiments on the growth of the plants in the greenhouse. The second part of the table is divided into two columns, the first column giving the results of the experiments on the growth of the plants in the open air, and the second column giving the results of the experiments on the growth of the plants in the greenhouse.

TO THE MEMORY
OF
THE VENERABLE
ALBERT ETHELBERT EBERT, Ph. M., Ph. D.,
THE NESTOR AND CHAMPION
OF
AMERICAN PHARMACY
THIS MODEST VOLUME IS RESPECTFULLY DEDICATED
BY
THE AUTHORS.

192868

PREFACE TO THE SECOND EDITION.

Eleven years have elapsed since the printing of the first edition, and so much progress has been made in the science of chemistry in the last decade that the manual had to be entirely rewritten. In revising the work, the author sought the aid of Professor Charles H. Kimberly, who has brought up to date the Inorganic part.

This book has been written for students of Pharmacy and prepared mainly from the hectographed lecture and laboratory notes which have been periodically distributed to our students.

When only a limited period of time is devoted to the study of chemistry, as is customary in pharmaceutical schools, it is, in the opinion of the authors, unwise to burden the student's mind with details of little bearing on Pharmacy. With this in view, they have based the text upon the United States Pharmacopœia. In no way, however, is the book designed to usurp the place of the national standard, to which it is intended as an introduction.

In the first chapters the elementary principles, such as definitions, nomenclature, notation, etc., are explained, followed by a discussion of the nonmetals. The next few chapters are devoted to the metals and their inorganic compounds, equation writing, stoichiometry, "periodic classification," etc.

The second part of the book is devoted to Organic Chemistry in which the classification and sequence are based on the excellent lectures of Professor Daniel C. Mangan. In this portion, the needs of pharmaceutical students have been kept constantly in view and all of the important "newer remedies" discussed with regard to their derivation and synthesis. Class reactions, syntheses and properties of entire classes are given wherever possible. The articles on elementary analysis, deduction of molecular formulas and toxicology, while brief, are complete.

The final *e* is dropped from the names of the halogens and binary compounds and organic compounds, but retained in the case of the alkaloids, and an arbitrary classification of the inorganic compounds into analytic groups has been attempted.

It is hoped that the book will take the place of the often incomplete and inaccurate lecture-room notes.

The thanks of the authors are due to Mr. Joseph L. Turner, who read the proofs of the organic part, to Miss Mary White Hutchinson, who has rendered valuable assistance in the preparation of the manuscript, and they wish to especially express their thanks to Professor George H. Meeker for his words of encouragement and for kindly placing at their disposal his valuable notes.

I. V. S. S.
C. H. K.

PHILADELPHIA, *November*, 1908.

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PHARMACEUTIC CHEMISTRY.

PART I.

INORGANIC CHEMISTRY.

CHAPTER I.

MATTER.

THE science of chemistry has been advanced so rapidly in recent years that it is almost impossible to keep pace with its progress. For this reason it has been divided into branches, each of which embraces or covers a special line of human endeavor. Thus, we have "Agricultural Chemistry," which deals with the problems of successful farming; "Metallurgical Chemistry," which deals especially with metals, their analysis and application in the arts. Why, therefore, should we not have "Pharmaceutical Chemistry," dealing with the chemistry of medicines.

It is justly held by some that "Chemistry is no less the same science, whether applied to metallurgy, medicine or pharmacy." But that after mastering the underlying principles, a certain branch of it should be specialized in, no one will deny.

GENERAL CONSIDERATIONS AND DEFINITIONS.

MATTER is that substance of which all bodies are composed. Thus, earth, wood, air, water, iron, gold, etc., are matter, though differing from one another in their properties.

Matter exists in *three states of aggregation*: (1) solids; (2) liquids; (3) gases.

Matter is impenetrable and indestructible. According to subdivision (size), it is divided into "*masses*," "*molecules*" and "*atoms*."

Any distinct portion of matter appreciable to the senses is called a *mass*.

The smallest portion of matter which can exist by itself and retain its peculiar characteristics is called a *molecule* (little mass).

The smallest particle of matter into which molecules can be divided is called an *atom* (not cut).

Atoms are hypothetical bodies, supposedly indivisible solids, with a definite, unchangeable weight and possessing a definite amount of attraction for other atoms which they neutralize and with which they unite.

An atom cannot exist by itself, but it unites with other atoms of the same kind to form molecules. Molecules, likewise, unite with other molecules to form masses.

When molecules of similar composition are attracted to each other, the force causing such attraction is termed *cohesion*; when, however, the

molecules are of unlike composition the force is called *adhesion*.

Atoms attract each other by a force known as *chemism* or *chemical affinity*.

CONTINUITY OF MATTER.—When a bar of iron is heated it expands; when cooled it contracts. The following reason for this change is given: It is assumed that the metal is composed of minute particles of matter which are not in absolute contact and which recede from each other upon the application of heat or approach each other when heat is withdrawn. That matter is not continuous can further be proven by the fact that when liquids of different densities are mixed (as, for example, alcohol and water) the bulk of the mixture contracts (shrinks). Thus, if 100 cubic centimeters of alcohol were mixed with 100 cubic centimeters of water, instead of having 200 cubic centimeters, as one would suppose, the mixture measures but 194 cubic centimeters. The loss in volume (bulk) of 6 cubic centimeters, or 3 per cent., shows clearly that between the particles of one of the liquids there must be open spaces which particles of the other liquid enter and thus cause the shrinkage.

There are many other proofs that matter is not continuous, but the above two familiar examples will, it is thought, suffice to show that matter is composed of exceedingly small particles which are not rigidly joined together, but which exist at some minute distances apart from one another; and, further, that these particles are in a state of constant motion

(vibration) which is increased by raising, and decreased by lowering the temperature of the substance. The minute particles referred to are called *molecules*, which we have already defined.

Since all compounds are made up of two or more substances into which they may be split, it follows that molecules must consist of smaller particles. Thus, if a molecule of hydrochloric acid be separated into its elements, we obtain a particle each of hydrogen and of chlorine—these smaller particles being the atoms referred to above.

Molecules of compounds may consist of any number of atoms; molecules of elements consist usually of only two atoms.

ELEMENTARY AND COMPOUND MATTER.—Matter may be either (1) simple or (2) compound.

When consisting of only one kind of elementary substance, as iron, copper, carbon, oxygen, etc., it is *simple matter*.

Compound matter consists of two or more kinds of matter in combination, as water, which consists of hydrogen and oxygen; or iron sulfate, which consists of iron, sulfur and oxygen, etc., and which are, therefore, *compounds*.

Simple matter—because it cannot be reduced with the means at our disposal to anything simpler—is called *elementary matter* or an *element*. An element, therefore, it is assumed, consists of but one kind of matter.

About eighty kinds of elementary matter or elements are known, and it is reasonable to suppose

that others remain to be discovered. Of these elementary substances combined in different proportion every kind of matter is composed. Indeed, the entire universe is constructed of elementary matter. Many of the compounds discovered in nature have been reproduced or duplicated in the chemist's laboratory and the list of compounds is constantly increasing.

SOLIDS, LIQUIDS AND GASES.—It has been stated above that matter exists in three forms. Any one of these three forms of matter can be converted into either of the other two. For example, ice is a solid, but when melted it becomes *liquid* (water). By boiling the liquid water, a *gaseous* vapor or steam is produced. All matter is influenced by two physical forces, the *force of attraction* (cohesion) and the *force of repulsion*, and according to the predominance of either of the forces, the different forms of matter result. Thus, when the force of attraction is greater, *solids* result; when the force of repulsion equals the force of attraction, we have *liquids*; when, however, the force of repulsion is greater than that of attraction, *gases* result.

PHYSICAL SCIENCE.—We cannot create or destroy matter, we can only alter its form and arrange differently the particles of which it is composed. We can, however, by study understand the changes which are taking place in nature.

The study of these changes in all their many forms is called "*Physical Science*."

PHYSICS is a branch of physical science which

treats of the phenomena of matter as such, without regard to its composition.

CHEMISTRY is the science which treats of the composition of bodies and the changes which this composition may undergo. Since chemistry reveals to us the secrets of the hidden particles, the term is thought to have its derivation in the Arabic word meaning "to conceal" (*kamai*).

Physics and chemistry are very closely allied, since nearly all chemical changes are accompanied by physical changes, and many physical changes involve chemical changes as well.

PHYSICAL AND CHEMICAL CHANGES.—A *physical change* is one in which the composition and properties of a substance are not permanently altered. A *chemical change* is one in which both the composition and properties of a substance are permanently altered and one or more new substances produced.

To illustrate these changes, we can take ordinary salt—sodium chlorid: It is a solid, but when placed in water it dissolves, losing its solid form. If we evaporate the water we obtain the salt in its original form, hence no permanent change took place. Such a change is called a *physical change*. If, however, we place the salt in sulfuric acid, while it again dissolves, on evaporation an entirely different compound results. A permanent change has taken place and a new compound possessing different properties has been formed. Such a change is known as a *chemical change*.

Chemical changes, also called *reactions*, when

expressed by means of symbols and signs are called *equations*.

Chemistry is divided into (1) *Inorganic* and (2) *Organic*.

INORGANIC CHEMISTRY treats of the metals and nonmetals, or materials coming from unorganized (mineral) sources.

ORGANIC CHEMISTRY is the study of carbon and its compounds. The older definition of organic chemistry, and the reason for its adoption as a separate classification, was due to the supposition that the class of compounds called "organic" originated in living tissue, hence of plant or animal origin. We know now that many such compounds can be made artificially from carbon and the inorganic elements. The term "organic chemistry," however, survived.

CHAPTER II.

GENERAL DISCUSSION.

IN order to conveniently study the elements which are of importance to the student chemist, it is necessary to classify them. Many systems of classification have been proposed, many purely arbitrary, but all open to criticism. Berzelius was the first to divide the elements into two large classes which he called "metals" and "metalloids."

The *metals* he considered to be those which possess luster and opacity, easily conduct heat and electricity, and are electro-positive in their combinations.

The *metalloids*—also called *nonmetals*—consist of gases, or if solids, possess no luster, ductility or malleability, are poor conductors of heat and electricity and are electro-negative in their combinations.

We know that this classification serves only in a general way, for a number of the elements are positive in one combination and negative in another; some metalloids possess a luster; some form alloys with metals; some form both acids and bases and, owing to these properties, may properly be placed in both divisions.

The most reasonable method of classification is by dividing the elements into groups, which is the system first proposed by Newlands, but later developed by Mendeleeff. This is the method most commonly

used. It is based upon the atomic weights and is known as the "*Periodic Law*." The system will be fully described in Chapter XVI.

This classification, also, has irregularities, but it seems to be the best at hand and has stood the test of years. Our method of grouping is very arbitrary. We, of course, retain the two divisions of—metals and nonmetals—but take up the study of nonmetals first, since it is by far the smaller group. The metals, however, we have grouped according to their behavior with reagents, which is considered most advantageous for the practical work of the pharmaceutic chemist.

COMPOUNDS AND MECHANICAL MIXTURES.—

These are differentiated as follows:

In a *mechanical mixture* there is no true union of the elements; in a *compound* there is. A *mixture* possesses all the properties of its ingredients, and these ingredients can be mixed in any arbitrary proportions. A *chemical compound*, on the other hand, possesses entirely different properties than the elements composing it, and its components are definite, fixed and invariable. Example: if iron is reduced in a mortar to the finest possible powder, and if ordinary sulfur, also in fine powder, is mixed with it intimately, the mixture will present a uniform appearance. If, however, a small quantity of it is placed under a microscope the particles of iron and sulfur will be found lying side by side. If we now use a magnet we can pick out the iron filings and leave the sulfur behind, or we can treat the

mixture with carbon disulfid which dissolves the sulfur and leave the iron behind. But, if a portion of the mixture is heated to redness, a chemical change occurs and a true compound is formed, in which neither the sulfur nor the iron can be revealed under the most powerful microscope. The product possesses properties unlike either of its composing elements and a magnet is now incapable of abstracting iron from it, and carbon disulfid will not dissolve out the sulfur. This is, therefore, an illustration of the fact that before heating it was simply a mechanical mixture, while after heating we had a true chemical compound (ferrous sulfid, FeS). Another proof that this is a chemical compound is that when it is treated with dilute sulfuric acid a gas possessing the odor of bad eggs is evolved. Neither the iron nor sulfur treated with sulfuric acid before they are combined will evolve this gas.

ELEMENTS AND COMPOUNDS.—As was said above, elements are bodies that have resisted all attempts to decompose them into simpler forms of matter. Thus, silver, gold, copper, are solid elements; bromin and mercury are liquid elements; hydrogen, oxygen, nitrogen, chlorin and fluorin are gaseous elements. Elements, therefore, exist in all three forms of aggregation.

A compound was defined as a body composed of two or more elements and is, therefore, capable of being split up into its components. Thus, mercuric oxid, HgO , is composed of mercury and oxygen, and by simply heating it, it is possible to resolve

it into mercury and oxygen, the first being a liquid metal, the latter a gas.

The elements are divided into two series: the nonmetals and the metals. There are sixteen non-metallic elements, the balance are all metals. All metals are capable of being polished. They possess a peculiar surface referred to as "metallic luster." They are all white to light blue or gray, with the exception of gold which is yellow and copper which is of a red color. The nonmetals, on the other hand, are destitute of the metallic luster, and such elements as phosphorus, sulfur and carbon are examples of the nonmetals.

SYMBOLS.—A symbol may be said to be a short-hand method of representing an element. For convenience in writing chemical reactions and for many other reasons these symbols are employed. They are usually the initial letters of the Latin name of the elements. Thus, H stands for hydrogen; O for oxygen; N denotes nitrogen; S sulfur; P phosphorus, etc. When more than one element have names beginning with the same initial letter, another characteristic letter is added. The first letter is always a capital, the second usually small. Thus, Hg for hydrargyrum; Os for osmium; Ni for nickel; Sb for stibium; Pb for plumbum.

ATOMIC AND MOLECULAR WEIGHTS.—The elements possess definite weights of their own. The atomic weights of the elements represent (a) the relative weights of the atoms compared with hydrogen; (b) the smallest quantity by weight which can

enter a chemical compound, this also compared with hydrogen; (c) the specific gravity of the element in the gaseous state as compared with hydrogen. The *atomic weight* of any element, therefore, is the number of times its atom is heavier than an atom of hydrogen. Hydrogen, being the lightest substance known, is generally used as the standard of weight for the elements. Its atomic weight is taken as *unity*; that is, it weighs one *microcrith*. When, therefore, we speak of oxygen having the atomic weight of 16, we understand it to weigh sixteen times as much as the hydrogen atom, or that it weighs 16 microcriths. In the same way we determine that the atomic weight of carbon is 12; nitrogen, 14; sodium, 23; potassium, 39; calcium, 40, etc.

Molecular weight of a compound is the sum total of the atomic weights in a molecule of the substance. Thus, CaO represents a molecule of calcium oxid, or common lime; from its formula we see it is composed of one atom each of calcium and oxygen. Now, the atomic weight of calcium is 40 and that of oxygen is 16. If we now add 40 and 16 we obtain the sum total of the atomic weights in the molecule, or 56; 56, therefore, is the molecular weight of calcium oxid. Common chalk, as another example, has the formula CaCO_3 . We find here a molecule composed of one atom of calcium which weighs 40; one atom of carbon, atomic weight 12; and three atoms of oxygen, atomic weight 16—taken three times, or 48. If we now add ($40 + 12 + 48 = 100$), the atomic weights of each of the elements in the

molecule, we obtain the sum of 100, which is the molecular weight of calcium carbonate, or chalk.

QUANTIVALENCE, ATOMICITY, VALENCE OR "BONDS."—By the valence of an element its atom-fixing power is meant. It may be defined as "the combining power of the atoms of an element as compared with that of hydrogen." It will be seen here that hydrogen is a unit of valence as well as a unit of weight. Atoms of certain elements have a combining power equal to the atoms of hydrogen. Thus, one atom of chlorine unites with one atom of hydrogen. Hydrogen, being the unit, has a valence of 1, and is called a *monad* or a univalent element. It therefore has 1 combining or replaceable "bond." Oxygen has a valence of 2, it is spoken of as a *dyad* and has 2 *combining* or replaceable *bonds*. Nitrogen is a *triad*, having 3 replaceable bonds; carbon, a *tetrad*, having 4 bonds, and phosphorus, a *pentad*, having 5 bonds. It will be seen that to neutralize the two bonds of oxygen two hydrogen atoms will be required, thus: —O— shows the two bonds of oxygen, and H—O—H shows these two bonds united to two monad hydrogen atoms, forming a "saturated" or "perfectly balanced" compound. Nitrogen, having three bonds, must be united with 3 hydrogen atoms in order to form a saturated

compound. Thus,
$$\begin{array}{c} \diagup \text{H} \\ \text{N} \text{---} \text{H} \\ \diagdown \text{H} \end{array}$$
 shows the nitrogen

atom to be saturated, giving rise to a compound having the formula NH_3 , and commonly called am-

monia gas, etc. Thus, it will be seen that elements can be divided according to their bonds or combining values into monads, dyads, triads, tetrads, pentads, hexads and heptads accordingly as they can replace 1, 2, 3, 4, 5, 6 or 7 hydrogen atoms or its equivalent in the molecule.

VARIABLE VALENCE.—While an element has always the same valence in the same compound, it may exhibit a different valence in different compounds. Thus, nitrogen, as has been seen in the case of ammonia, exhibited the valence of 3. In nitric acid, however, and in all the nitrates it is always 5. Many other elements have this variable valence. Thus:

Sulfur, Chromium, Manganese act as dyads, tetrads and hexads.

Arsenic, Antimony, Phosphorus act as triads and pentads.

Carbon acts as dyad and tetrad.

Iron acts as dyad and triad.

Tin acts as dyad and tetrad.

CHEMICAL FORMULAS.—A formula is an expression of the composition of a molecule. It consists usually of two or more symbols written together, and represents a definite molecular weight. If water, represented by the formula H_2O , is taken for example, it is seen to be composed of two parts by weight of hydrogen and 16 parts by weight of oxygen; the molecular weight of water, therefore, is 18. KCl is the formula for potassium chlorid and represents 74.4 parts of potassium chlorid, which is the sum total of 39, the atomic weight of potassium, and 35.4.

the atomic weight of chlorin. When we desire to represent more than one atom of an element it is necessary to affix a small numeral at the lower right-hand corner of the symbol representing the element. Thus Na_2 represents two atoms of sodium, or 46 parts of sodium by weight. In the same way O_3 represents 3 times the atomic weight (16), or 48 parts of oxygen by weight.

Common soda has the formula Na_2CO_3 ; if we wish to represent more than 1 molecule of common soda, we place a large numeral before the formula. Thus, $3\text{Na}_2\text{CO}_3$ represents 3 molecules of soda, the 3 multiplying each of the atoms in the molecule. 4HCl represents 4 molecules of hydrochloric acid and stands for 4 hydrogen and 4 chlorin atoms. $2\text{H}_2\text{SO}_4$, on the other hand, is the formula of two molecules of sulfuric acid and it stands for 4 atoms of hydrogen, 2 atoms of sulfur and 8 of oxygen. Thus the numeral placed before the molecule multiplies all the atoms in the molecule, while a numeral placed after a symbol multiplies only that one symbol.

If a group of symbols (NH_4) is followed by a numeral, the whole group is multiplied by that numeral. Thus, $(\text{NH}_4)_3$ stands for 3 molecules of ammonium; $(\text{NO})_4$ stands for 4 molecules of nitric oxid, etc.

CLASSIFICATION OF COMPOUNDS.—Compounds are classified into bases, acids and salts.

Bases are the hydroxids of the metals. Some bases are soluble, others not. The soluble bases have a caustic taste and turn red litmus paper blue. Slaked lime is a common example of the bases.

Acids are defined as the salts of hydrogen. They have a sour taste, are corrosive and turn blue litmus red.

Salts are acids in which part or all the basic hydrogen has been replaced by a metal. Salts are named after the element and the acid from which formed. Thus, if potassium replaces the hydrogen of sulfuric acid—potassium sulfate is formed.

The salts are usually classified or subdivided into normal, acid, basic and double salts.

A *normal* salt is an acid in which all the basic or replaceable hydrogen has been replaced by a metal, as in potassium tartrate ($K_2C_4H_4O_6$).

An *acid* salt is one in which not all of the basic hydrogen of the acid has been replaced, as in potassium bitartrate ($KHC_4H_4O_6$).

A *basic* salt is an acid in which part of the hydrogen has been replaced by a metal and another part by an oxid or a hydroxid. Thus, basic lead acetate (lead subacetate) serves a good example: $Pb(PbO)(C_2H_3O_2)_2$.

A *double* salt is an acid in which the basic hydrogen is replaced by two metals. Example: Potassium, sodium tartrate (Rochelle salt)— $KNaC_4H_4O_6$.

CLASSES OF ACIDS.—The acids are divided into those containing no oxygen, which are termed *hydracids*, and those containing oxygen which are termed *oxacids*. The names of all hydracids begin with the prefix *hydro* and the names of their salts end with the suffix *id* (ide). Examples: Acid hydrochloric, acid hydriodic, acid hydrobromic, acid

hydrosulfuric. Such well-known acids as sulfuric, nitric and oxalic belong to the class of oxacids. In the oxacids the quantity of oxygen present in the acid determines their names. Thus, names of acids containing least oxygen begin with *hypo* and end in *ous*. Those containing the next larger quantity of oxygen end in *ous* omitting the *hypo*. The next higher acid ends in *ic*, while the highest acid begins with *per* and ends in *ic*. The following chlorine oxacids serve as examples: Hypochlorous acid (HClO), chlorous acid (HClO_2), chloric acid (HClO_3), perchloric acid (HClO_4).

CLASSIFICATION OF THE NONMETALS.

The nonmetals, grouped according to their valences, are as follows:

GROUP	SYM- BOL	VALENCE	AT. WT.
Hydrogen Group:			
Hydrogen	H	1	1.0
Chlorin Group:			
Chlorin	Cl	1, 3, 5	35.4
Bromin	Br	1, 3, 5	79.8
Iodin	I	1, 3, 5	126.5
Fluorin	F	1	19.0
Sulfur Group:			
Oxygen	O	2	15.88
Sulfur	S	2, 4, 6	31.98
Selenium	Se	2, 4, 6	79
Tellurium	Te	2, 4, 6	128
Nitrogen Group:			
Nitrogen	N	3, 5	14
Boron	B	3	10.9
Phosphorus	P	3, 5	30.9
Carbon Group:			
Carbon	C	2, 4	11.97
Silicon	Si	2	28.3

CHAPTER III.

THE NONMETALS.

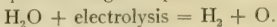
HYDROGEN.

A GASEOUS element. Symbol, H. Atomic weight, 1. Molecular weight, 2. Valence, 1. Density, 1. Weight of one liter = 0.0899 gm. (0.09). One gram of hydrogen at 0° C. and 760 millimeters pressure will occupy 11.16 liters of space.

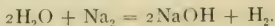
Occurrence.—Hydrogen was discovered by Cavendish (1766). It occurs in the free state in gases from volcanoes, several semi-active fumaroles and in the atmosphere of the sun. In combination it is a constituent of water and in most organic substances of both animal or vegetable origin. It is a necessary constituent of all acids, bases and ammoniacal compounds. Does not exist free on the earth, but has been found free in meteorites which have fallen upon the earth.

Preparation.—Hydrogen is produced by the following methods:

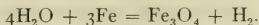
(1) Electrolytic decomposition of water; hydrogen collecting upon the negative pole.



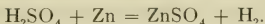
(2) By the action of metallic sodium or potassium on water.



(3) Action of steam on red-hot iron.



(4) Chemical reactions. Decomposition of mineral acids by a metal, usually zinc or iron, and dilute sulfuric acid.



This latter method is usually employed in laboratories. Dilute sulfuric acid is used to prevent the crystallization of the zinc sulfate produced. If absolutely pure zinc is used, no action will take place unless an electric current is passed through the solution. Since commercial zinc is usually employed, the hydrogen obtained is not entirely pure, but contains some other gases derived from the impurities of the zinc.

Properties.—When pure and at normal temperature and pressure, hydrogen is a colorless, transparent, odorless and tasteless gas. It is invisible, combustible, but does not support combustion. Burns with a pale-blue flame, forming water. Hydrogen produces more heat than any other known substance, weight for weight. It is 14.5 times lighter than air, and is the lightest substance so far known. It is almost insoluble in alcohol, and at a temperature of -240°C and a pressure of 650 atmospheres, it has been liquefied to a steel-blue liquid. It has not been permanently liquefied, however, and is practically the only gas that has not been so condensed. Its boiling-point is stated as -243°C ., and its critical temperature, -233°C . It is the best conductor of heat and electricity among the gases

It is very diffusible, passing through most glasses slowly, but is chemically inactive under ordinary conditions. It is nonpoisonous, but will not support respiration of animals.

It will readily unite acids with other elements at the moment of its formation (nascent state).

Its use in nature is to assist in formation of water and of vegetable and animal tissues.

In the arts hydrogen is used for heating and illuminating purposes, as a lifting power in balloons, etc., but its uses are quite limited. The oxyhydrogen blowpipe offers a means of employing its great heat value (3000°C.).

In the laboratory it is the ideal reducing agent, and is widely used as such.

Compounds.—With oxygen it forms hydrogen monoxid—water, H_2O . (For description of waters, see Chapter VI.) It also forms hydrogen peroxid, H_2O_2 , a colorless, odorless liquid with an astringent taste which acts as an oxidizing agent, but may also act as a reducing agent. Hydrogen dioxid (peroxid) decomposes readily, even spontaneously, and is now best preserved by adding 0.2 % of acetanilid. Used as a bleaching agent, disinfectant and antiseptic. Also as a cleansing and oxidizing agent.

OXYGEN.

History.—Oxygen was independently discovered by Priestley in England in 1774 and by Scheele in Sweden at the same time, though Scheele's results were not published until 1775.

Priestley was heating some red mercuric oxid under a reading-glass by concentrating the sun's rays upon it, when it changed to metallic mercury and liberated a gas. He called this gas "dephlogisticated air." Scheele obtained his oxygen by heating "braunstein" (dioxid of manganese), and called it "empyreal air" on account of its power of supporting combustion.

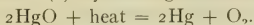
A few years later, Lavoisier proved both gases to be identical and applied the present name oxygen (the name meaning—producing sour), from the erroneous idea he had, that oxygen was necessary to acid production.

Occurrence.—Oxygen is present in the air mixed with about four times its volume of nitrogen and other gases.

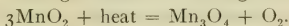
Combined, it is the most abundant element, composing $\frac{8}{9}$ of water and almost $\frac{1}{2}$ of rocks composing the earth's crust, also in vegetable and animal tissues.

It is present in nearly all natural substances and almost everywhere.

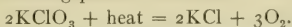
Preparation.—(1) By heating red mercuric oxid.



(2) By heating black oxid of manganese.

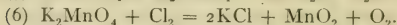
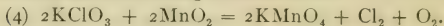


(3) By heating potassium chlorate.



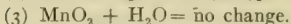
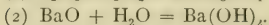
If manganese dioxid and potassium chlorate are mixed and heated, the oxygen is given off at a much lower temperature, the potassium chlorate giving up the oxygen, the manganese dioxid re-

remaining unchanged, merely acting as a *catalyzing agent*. Catalytics *enhance chemical reaction* without themselves becoming involved in it.



Physical Properties.—Oxygen is a colorless, tasteless and odorless gas. It is slightly heavier than air and 16 times as heavy as hydrogen. One liter of the gas under standard conditions weighs 1.43028 gms. It is slightly soluble in water, thus affording the oxygen for the respiration of water animals and plants. Oxygen can be liquefied under reduced temperatures and increased pressure.

It does not burn, but supports combustion. Unites with all elements but fluorin, forming oxids of three classes. *Acid oxids* are those which, when added to water, produce acids. *Basic oxids* are those which, when water is added, produce bases. *Neutral oxids* do not form either bases or acids with water. Examples:



Oxygen possesses very powerful properties chemically. Most of the natural atmospheric changes are due to oxygen.

Its chief function is to support combustion. The greatest type of combustion is that of respiration—in which we take air into the lungs, separate the oxygen and eliminate it from the body in the form of

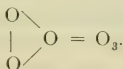
carbon dioxid, CO_2 . It assists in the burning up of waste tissues in the blood.

Chemically, oxygen is the typical oxygenizing agent. It is used in the oxyhydrogen blowpipe to produce intense heat, and with lime, intense light.

Oxygen plays its part medicinally as a stimulant and tonic. *Ozone* is an allotropic form of oxygen.

Ozone was discovered in 1785 by Von Marum and called electrified oxygen. Schönbrein in 1840 determined its composition.

When air or oxygen is exposed to the action of electric sparks, it undergoes a peculiar change, acquiring a strong, pungent odor, contracting in volume and exhibiting other new properties. Ozone may also be obtained by several other means. It has a density of 24, a molecular weight of 48, and is represented by the graphic formula:

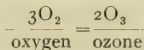


It is present in the atmosphere one part in 700,000.

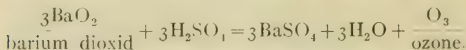
The peculiar power that certain elements thus have of assuming more than one form is known as allotropy.

The properties of ozone are those of oxygen, but intensified.

Preparation.—(1) By subjecting oxygen to low temperature and high pressure:



(2) In dilute form, by acting with strong sulfuric acid on barium dioxid:



The compound of oxygen and hydrogen constitutes water, H_2O , which will be discussed in Chapter VI.

NITROGEN.

A gaseous element. Symbol, N. Atomic weight, 14. Valence, 3 or 5. Density, 14. One liter weighs 1.256 grams.

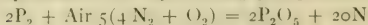
Occurrence.—Nitrogen exists free in the air mixed with oxygen, argon, etc.; also free in the gases of the stomach, intestines, blood, urine, etc. Combined, it occurs as nitrates of potassium, sodium and calcium in animal and vegetable tissue and in ammonia compounds.

History.—It was discovered in 1772 by Rutherford, who called it “mephitic air” (meaning poisonous to life). Lavoisier called it azote for the same reason. Scheele first recognized it as a constituent of air.

The present name, nitrogen, was suggested by Chaptal, on account of its being a constituent of niter, hence a “niter producer.”

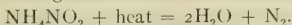
Properties.—Nitrogen is a colorless, odorless, tasteless, invisible gas; neither combustible nor a supporter of combustion; nonpoisonous, will not support life. Soluble in water, lighter than air; chemically very inert.

Preparation.—(1) By burning phosphorus in air.



The P_2O_5 (phosphoric anhydrid) is then absorbed by water, the impure nitrogen remaining.

(2) By heating ammonium nitrite to decomposition.



The nitrogen so obtained being pure.

Function.—To dilute the oxygen of the air, to assist in plant growth and animal-tissue formation and is of great value in many ways in the form of its compounds of nitrogen.

With hydrogen it forms *Ammonia*, NH_3 .

A colorless, pungent, irrespirable gas, freely soluble in water, lighter than air, liquefied easily, it emulsifies, but does not saponify fats.

Ammonia is found usually in very small quantities, but universally distributed in the atmosphere, rain water, soil, sewer gases, urine, etc. It is produced naturally by dissociation of organic compounds of nitrogen by the action of bacteria. Its chief commercial source is the "ammoniacal liquor" from gas-works.

With oxygen it forms five oxids:

(1) Nitrous oxid, N_2O . Laughing gas.

(2) Nitric oxid, N_2O_2 .

(3) Nitrogen trioxid, N_2O_3 . Nitrous anhydrid.

(4) Nitrogen tetroxid, N_2O_4 .

(5) Nitrogen pentoxid, N_2O_5 . Nitric anhydrid.

The important oxids are N_2O , N_2O_3 and N_2O_5 —these forming the following oxacids:

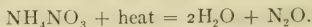
(1) $N_2O + H_2O = 2HNO$. Hyponitrous acid.

(2) $N_2O_3 + H_2O = 2HNO_2$. Nitrous acid.

(3) $N_2O_5 + H_2O = 2HNO_3$. Nitric acid.

The most important of these latter compounds is nitric acid and from it the others are obtainable. It will be fully described under Acids, Chapter VIII.

Nitrogen monoxid, N_2O , discovered by Priestley in 1793. A colorless, odorless, nearly tasteless gas. Incombustible, but supporting combustion, respirable to a limited extent. Obtained by heating ammonium nitrate:



Used as an anesthetic in dentistry and minor surgery since 1845.

Nitrogen trioxid, N_2O_3 , unites with water to form nitrous acid and hence produces nitrites in natural combination. It has been proven not to exist in a gaseous condition, but to consist of a mixture of nitrogen oxids.

Nitric anhydrid or *nitrogen pentoxid*, N_2O_5 is a white, solid substance at low temperatures and decomposes at 45° , evolving brown fumes of N_2O_3 .

When added to water, it produces nitric acid, HNO_3 , called *aqua fortis* (strong water).

CARBON.

A solid, multiform element. *Symbol*, C. *Atomic weight*, 12. *Valence*, 4.

Occurrence.—Found both free and in combination. All carbon except the incombustible owes its origin to animal or vegetable life.

Free, it is found in three distinct forms: (1) diamond, (2) graphite, (3) amorphous carbon. All varieties are insoluble and infusible, but readily com-

bustible, having a strong affinity at high temperatures for oxygen, and burning to form CO_2 . All but the diamond are good conductors of electricity.

(1) *Diamond*.—This is pure carbon when colorless; but with certain small quantities of impurities present, the color may be found to be yellow, blue or even black. It is found in but few places, the most important being the South African diamond fields of Kimberley, where it occurs in a blue cement rock filling the craters of extinct volcanoes. It is also found in some meteorites and very small crystals have been obtained artificially.

It is probably due to vegetable origin, the change taking place at intense temperature and great pressure during great length of time. It is the hardest of all substances known, hence finds much use as a cutting and grinding material. The brilliancy as a gem is due to its high refractive power. The diamond itself is cut or polished by the use of diamond powder.

(2) *Graphite*, also called plumbago and black lead, is pure carbon of vegetable origin crystallizing in six-sided plates. Found in largest quantities in Ceylon and New York State. Is black in color, lustrous, and is used for lead-pencils, lubricants, crucibles, stove polishes and for electrotyping, is infusible and not easily burned. In crucibles, pencils, etc., it is mixed with varying proportions of clay. It is made artificially by heating coal mixed with powdered iron ore to a very high temperature by means of the electric current.

The amorphous forms are obtained artificially in the form of coke, charcoal, both animal and wood, and lampblack or oil charcoal.

The amorphous forms of carbon: Naturally, we find these forms of coal all of vegetable origin resulting from the effect of enormous pressure and heat, accompanied by a peculiar fermentation, by means of which the oxygen and other elements have been nearly driven off, leaving nearly pure carbon.

In *anthracite* the process has progressed much farther than in bituminous coal, and is nearly pure carbon with small quantities of hydrogen and oxygen. *Bituminous coal* contains considerable hydrocarbon compounds.

Cannel coal is a resinous variety.

Lignite is still more recent and shows even the cellular structure of the wood which was its origin.

Peat is partially decomposed moss.

Petroleum contains compounds of carbon and hydrogen. It is quite largely distributed throughout the world. It varies very much in appearance and properties, but is usually dark in color and very odorous, often due to sulfur and nitrogen compounds.

Artificially, we obtain impure carbon, as charcoal, of several forms:

(1) *Charcoal*.—Wood charcoal, obtained by burning wood with insufficient supply of oxygen, whereby the most readily combustible materials are burned, leaving about 19% of nearly pure carbon. Animal charcoal is similarly made by combustion of bone and

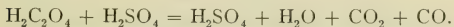
is known as bone-black, drop-black, but contains only about 10% of carbon, the rest being bone-ash, or calcium phosphate, used in sugar refining.

Coke is made by a similar combustion or distillation of coal, used for iron making. The by-products of coke manufacturing are now separated and find large commercial value.

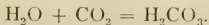
Lamp-black is prepared by insufficient combustion of petroleum, gas or similar organic substances. It is used as a black pigment, especially in printers' ink, which consists of lamp-black, linseed oil and soap as its chief ingredients.

In combination, carbon is also present in carbonates, bicarbonates, carbon dioxid gas and in all organic substances, whether of animal or vegetable origin.

Compounds with oxygen: *Carbon monoxid* gas, CO, not native, colorless, slight odor, very poisonous. Nonsupporter of combustion, combustible, slightly soluble in water. Prepared from oxalic acid:

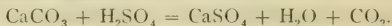


Carbon dioxid, or anhydrid, CO₂, is a colorless, odorless gas, soluble in water, nonsupporter of combustion and incombustible. Occurs free in air and many waters, and is formed during respiration, combustion, decay and most fermentations. With water it is supposed to form carbonic acid, which is very unstable:



The carbonates of the metals are very important

and very abundant. Carbon dioxid is usually prepared from marble:



Preparations of C with nitrogen we have the cyanogen compounds—very poisonous: C_2N_2 , cyanogen is a colorless gas, with a characteristic odor, combustible with a pink flame; HCN, or prussic acid, a liquid, colorless, volatile, feeble acid, with odor of bitter almonds, prepared by acting on potassium cyanid with dilute sulfuric acid:



Acid hydrocyanic dilute, U. S. P., contains 2% absolute HCN. *Scheele's prussic acid* contains 4%.

CHAPTER IV.

THE HALOGEN ELEMENTS.

THE halogen group is so named because of the close resemblance between their sodium salts and sea salt, the term *halogen* signifying "salt producer." The group comprises *iodin*, *chlorin*, *bromin* and *fluorin*, which in their general characteristics strongly resemble each other and readily change places in combinations without producing any very marked change in the character of the compound.

They are electronegative, fluorin being most strongly so and iodin the least so. They have a characteristic pungent odor and act as disinfectants and bleaching agents. They exhibit a regular physical gradation with increase in atomic weight. Thus fluorin and chlorin are gases, bromin is a liquid and iodin is a solid under normal conditions.

Chemically, they show the same gradation of change; with hydrogen, fluorin unites instantly and so eagerly as to produce explosion by mere contact, even in the dark. Chlorin will not unite with hydrogen except in the light, but in direct sunlight does so rapidly, producing explosive tendencies. Bromin vapor requires a flame to produce union with hydrogen, and iodin vapor and hydrogen require to be strongly heated in contact with spongy platinum.

With oxygen they unite quite difficultly and in inverse order. The compounds formed are rather unstable. Bromin and fluorin have no oxids.

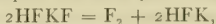
Fluorin produces no oxacids or salts. Thus, the compounds formed are:

Hydracids.	Oxids.	Oxacids.
HF:		
HCl:	Cl_2O Cl_2O_3 Cl_2O_5 :	HClO HClO_2 HClO_3 HClO_4
HBr:		HBrO HBrO_3 HBrO_4
HI:	I_2O_3 I_2O_5 :	HIO HIO_2 HIO_3 HIO_4

FLUORIN.

Fluorin is the typical group element: Valence, 1. Density, 19. Atomic weight, 19. Specific gravity, 1.3.

History.—Very recent in its discovery, for it was not possible to isolate it until 1886, when Moissan finally succeeded. He obtained fluorin by passing an electric current through a solution of potassium fluorid, FK, in anhydrous hydrofluoric acid, HF. Fluorin he separated at the anode, with hydrogen at the cathode, the reactions taking place thus, the breaking up of the acid potassium fluorid:



The reaction is carried out in a U-tube of platinum-iridium, this being acted upon less than platinum alone.

Occurrence.—Fluorin occurs in combination in considerable quantities as native *fluor-spar*, CaF_2 , and in *cryolite*, Na_3AlF_6 , and other similar compounds; also in small amounts in bone, tooth enamel and some mineral waters.

Properties.—Of all known elements, fluorin is the most active, due to its intense chemical affinities.

It resisted long any attempt to isolate it, for if liberated, it instantly recombined with the materials of the vessel in which the separation was made.

It appears to be a colorless gas, with a characteristic irritating odor; but even this is of doubtful truth, for with the moisture of the air or of the mucous membranes hydrofluoric acid is instantly produced, hence the true odor of fluorin is not certainly known. All metals, even gold and platinum, are acted on by fluorin to a greater or less extent and organic compounds are attacked violently. At a temperature of -185° , it condenses to a liquid condition. This was obtained also by Moissan and Dewar in 1897.

The liquid is a yellowish, mobile fluid, having no action on silicon, phosphorus, sulfur or glass. It attacks, however, hydrogen and hydrocarbons freely, combining violently with all elements except oxygen, nitrogen and chlorin.

Compounds.—Hydrogen fluorid or *hydrofluoric acid* is prepared by the action of strong sulfuric acid on calcium fluorid, thus:



The gaseous acid is passed into water in leaden, wax or gutta-percha bottles as it attacks glass. The anhydrous acid is prepared by heating acid potassium fluorid in platinum retorts, thus:



It is a colorless, limpid, fuming liquid, boiling at 19° C. It is used as a solvent of glass in etching, etc. It is exceedingly dangerous to handle, for it produces not only irritation to mucous surfaces, but

severe burns upon the flesh and often serious constitutional symptoms and death.

CHLORIN.

At. wt., 35.5. Valence, 1-3-5-7. Sp. gr., 2.47. Density, 35.4. Symbol, Cl.

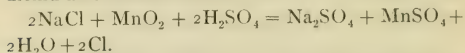
History.—Discovered by Scheele in 1774 and thought to be a compound of oxygen and hydrochloric acid. He called it “dephlogisticated marine acid gas,” for hydrochloric acid was then known as “marine acid.” In 1810, Davy gave it the name chlorin, on account of its greenish-yellow color.

Occurrence.—Always in combination and very abundantly. The most common form being sodium chlorid.

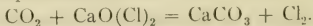
Preparation.—(1) By action of hydrochloric acid on manganese dioxid.



(2) By action of sulfuric acid on manganese dioxid and sodium chlorid.



(3) Slowly generated when moistened chlorinated lime is exposed to the air.



Properties.—A greenish-yellow gas 2.5 times as heavy as air, pungent and suffocating odor. Irrespirable, irritating, soluble in water. One volume of water at 10° C. dissolves 3 volumes of gas. Liquor chlori compositus, U. S. P., is a 0.4% solution.

Liquid chlorin is now a commercial article and is

used in extraction of gold from its ores. Sp. gr. 1.33; boils at 33.6°C .

Chemically, chlorin is very active and especially noted for its affinity for hydrogen and the metals with which it forms chlorids. Burns in an atmosphere of hydrogen. Its allotropic form is similar in appearance, but is inactive. It is prepared in the dark. The well-known bleaching property of chlorin depends upon its affinity for hydrogen, it decomposes the moisture liberating oxygen which in its nascent state energetically decomposes the coloring matters.

Chlorin will not bleach a perfectly dry substance.

Compounds.—With oxygen—none important:

Cl_2O , chlorin monoxid.

Cl_2O_3 , chlorin trioxid.

Cl_2O_4 , chlorin tetroxid.

With oxygen and hydrogen it forms the acids of chlorin:

HCl , hydrochloric acid, a hydracid.

HClO , hypochlorous acid.

HClO_2 , chlorous acid.

HClO_3 , chloric acid.

HClO_4 , perchloric acid.

} oxacids.

The important acids are HCl , HClO , HClO_3 and will be further discussed in Chapter VIII.

BROMIN.

Symbol, Br. At. wt., 79.76. Sp. gr., 2.99. Valence, 1.

History.—Discovered by Balard (1826), in the sea-water after crystallizing out the salt from con-

centrated solution. He gave it the name bromin (bromos, signifying a stench), on account of its disagreeable odor.

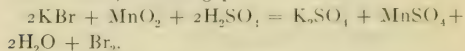
Occurrence.—Never free in nature. Chiefly combined with the alkaline metals and magnesium in sea-water and in many saline and salt springs. The saline deposits of Stassfurt contribute a large part of our bromin supply.

Preparation.—Sea-water, or other saline brine, is evaporated and several crops of the less soluble materials collected. The final liquid known as "bittern," is treated with chlorin gas which liberates bromin, thus:



This is then shaken out with ether, removed, treated with potassium hydroxid and evaporated to dryness, leaving potassium bromid and bromate.

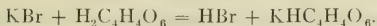
This is then treated with manganese dioxid and sulfuric acid, liberating pure bromin.



Properties.—A heavy, dark-red, mobile liquid, evolving at ordinary temperature a reddish, irritating, pungent odored gas. Soluble in thirty parts of water and readily soluble in alcohol, ether and chloroform. Chemical properties similar, but weaker than those of chlorin. Poisonous. Recognized by its color and by its odor, also by the yellow color of its solutions. Is separated from its compounds by chlorin, and may be so identified. Impurity usually present is bromin chlorid, BrCl .

Compounds.—Similar to chlorin compounds, but less stable.

Hydrogen bromid or hydrobromic acid, HBr , is made by action of potassium bromid and tartaric acid.



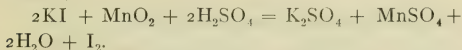
See chapter on Acids, page 71.

IODIN.

Symbol, I . At. wt., 126.54. Sp. gr., 4.95. Valence, 1.

History.—In 1812, Courtois was endeavoring to prepare niter from the ashes of sea-weeds. He noticed the beautiful violet-colored vapors. It remained for Guy Lussac, however, to investigate it later on. It derives its names from the color of its vapor.

Occurrence.—Similar to the other members of this group, it is never found in nature as an uncombined element. It is associated with the alkali metals, with magnesium and calcium. Found in niter beds, in sea and mineral spring waters, but most largely in certain sea-weeds collected off the coast of Scotland and France, and from the ash of these weeds our commercial supply largely comes. This ash is obtained at as low a temperature as possible and is known as "kelp." For laboratory uses iodine can be obtained in the same manner as chlorine, thus:



Properties.—A bluish-black, shining crystalline

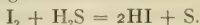
solid. Crystallizes in scales or tablets, emitting an irritating vapor. Melts at 114° C. It is poisonous, and used as external anodyne. Its salts are alterative when used internally.

Free iodin turns starch paste blue and may be rendered free from its compounds by chlorin gas. Acetate of lead gives a yellow precipitate of lead iodid with compounds of iodin;

The preparations in common use medicinally, are: tincture iodin, a 7% alcoholic solution, containing potassium iodid;

Liquor iodi compositus (*Lugol's solution*) solution, of iodin and potassium iodid in water: 5 gms. iodin, 10 gms. potassium iodid, in 100 gms. of the solution;

Hydriodic acid, HI, made by passing hydrogen sulfid gas through an iodin solution.



Syrup hydriodic acid contains 1% HI. Made by reaction of potassium iodid and tartaric acid in alcoholic solution.



The chemical compounds are similar to those of bromin, but fewer in number and less stable.

CHAPTER V.

THE SULFUR GROUP.

THE sulfur group consists of sulfur, silicon, phosphorus, boron, selenium and tellurium. The important members of this group are sulfur, phosphorus and boron. Silicon is worthy of some consideration, while selenium and tellurium are of little importance to the pharmaceutic chemist. Sulfur, as the most important, will be considered first.

SULFUR.

Symbol, S. Sp. gr., 2. At. wt., 31.85. Melts at 115° C.

History.—Sulfur was known to the ancients.

Occurrence.—Occurs free in volcanic areas, and our most important source has long been Sicily and Italy. Large deposits are found in Iceland, China, India, California and the Rocky Mountain districts. It usually occurs mixed with clay, from which it may be separated by distillation. Beds are found sometimes in which the sulfur is constantly being formed, due to chemical changes, and such beds are called "sulfatara."

It is also found in many ores in combination with metals, as sulfids and sulfates, also in many mineral springs, both free and as sulfids, sulfates or

even as sulfuric acid; also in many organic plant and animal bodies.

Properties.—Sulfur, when pure, is a solid, pale yellow, dimorphous, with several amorphous modifications. Melts at 115°C ., boils at 448°C . Brittle, nearly tasteless and odorless, nonconductor of heat and electricity. Insoluble in water, and almost so in alcohol; best solvent is carbon disulfid, 100 parts of which dissolves 37 parts of sulfur. In relation to its *forms*, sulfur may be divided into two classes:

A. Those soluble in carbon disulfid.

A. (1) Yellow, opaque, rhombic octahedra.

(2) Long, transparent, needle-shaped prisms; these return to the octahedra after a few days' exposure.

(3) A variety of lac sulfur, prepared by acting on alkaline polysulfids with a mineral acid.

B. Those insoluble in carbon disulfid.

B. (1) A tenacious, amorphous mass, obtained by pouring sulfur heated to 230°C . into cold water.

(2) A variety of lac sulfur prepared by acting on a thiosulfate with dilute mineral acid, or along with flowers of sulfur that are suddenly cooled.

Preparation.—Nearly all obtained from native sulfur by distillation. A small amount from iron pyrites. In laboratory practice it may be prepared by several means, such as the reaction of hydrogen sulfid and sulfur dioxid:



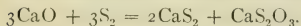
Also by burning hydrogen sulfid with insufficient supply of air, thus:



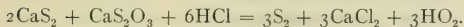
Sulfur is also a by-product in smelting of copper pyrite and in the vat waste of the LeBlanc process of preparing sodium carbonate.

Official sulfurs and preparations: Sublimed sulfur, flowers of sulfur, obtained by vaporizing and condensing sulfur. This is not pure, contains possible impurities and sulfurous and even sulfuric acid. In order to insure purity, it is treated with ammonia water, which neutralizes the sulfur acids, removes the arsenic which it dissolves out, and other impurities and produces a pure sulfur. This is known as *washed sulfur*, and is preferred by many for medicinal purposes.

Precipitated sulfur is lighter, more easily suspended in liquids and hence preferable to the other forms. It is prepared by boiling together sublimed sulfur and lime, filtering and adding hydrochloric acid.



calcium
thiosulfate



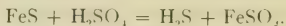
The precipitated sulfur is thoroughly washed with water.

If sulfuric acid is used in place of the hydrochloric acid, the precipitate is contaminated with calcium sulfate, and it then goes by the name of "milk" or "lac sulfur."

Sulfur iodid is prepared by rubbing together sulfur and iodine and heating. The product is in the form of a grayish-black solid and is quite unstable and decomposes readily.

Compounds.—With hydrogen:

Hydrosulfuric acid, H_2S , also called hydrogen sulfid or sulfuretted hydrogen. A strong colorless gas, of characteristic odor, soluble in water, produced naturally in organic decay when sulfur is present. Also found in many mineral springs. May be prepared by acting on iron sulfid with dilute sulfuric acid.



With oxygen:

Sulfur dioxid, SO_2 = sulfurous anhydrid.

Sulfur trioxid, SO_3 = sulfuric anhydrid.

With oxygen and hydrogen:

H_2SO_2 , hyposulfurous acid.

H_2SO_3 , sulfurous acid.

H_2SO_4 , sulfuric acid.

$\text{H}_2\text{S}_2\text{O}_3$, thiosulfuric acid.

$\text{H}_2\text{S}_2\text{O}_7$, pyrosulfuric acid.

$\text{H}_2\text{S}_2\text{O}_6$, dithionic acid.

$\text{H}_2\text{S}_3\text{O}_6$, trithionic acid.

$\text{H}_2\text{S}_4\text{O}_6$, tetrathionic acid.

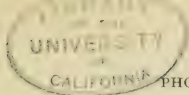
$\text{H}_2\text{S}_5\text{O}_6$, pentathionic acid.

The important ones are sulfuric, thiosulfuric and pyrosulfuric, which will be discussed under Acids, Chapter VIII.

PHOSPHORUS.

Symbol, P. At. wt., 31. Sp. gr., 1.83 at 10°C .

History.—Phosphorus was discovered by Brandt, of Hamburg, in 1669, in urine; by Boyle in 1680, by a secret process; in 1769, by Gohn, in bones; and until



1771, when Scheele published a method of obtaining it from bone ash, phosphorus was considered a chemical curiosity.

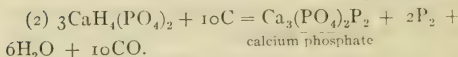
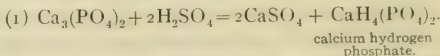
Occurrence.—It has never been found free in nature; in combination it is most common as calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, a mineral derived from the bones of the prehistoric mammals. Occurs in soils and in animal bones, tissue and blood. Also in plants to which it is also essential.

Properties.—Elementary phosphorus is a solid occurring in two forms: (1) Yellow phosphorus, soft and flexible, insoluble in water, soluble in oils and carbon disulfid. Poisonous, volatile and inflammable, even at low temperatures, fusible and luminous in the dark. Combines readily with oxygen. (2) Red or amorphous phosphorus, opaque, insoluble in carbon disulfid, infusible and nonluminous and possessing no tendency to combine with oxygen. At a temperature of 260°C. , it is changed into ordinary phosphorus and assumes its properties. Red phosphorus is prepared by heating the ordinary variety for about 36 hours to a temperature of 250°C. without supply of oxygen.

Other varieties have been prepared. The metallic or black form is prepared by heating red phosphorus in a sealed tube to 500°C. It is inert and of no importance. Ordinary phosphorus must be kept under water to prevent spontaneous combustion, its most characteristic property being its ready oxidation.

Preparation.—Phosphorus is obtained from cal-

cined bones by adding sulfuric acid, filtering, removing the calcium sulfate; the liquid evaporated, and residue distilled with charcoal, thus:



Compounds.—With hydrogen:

PH_3 , phosphorus trihydrid, phosphoric or phosphoretted hydrogen, phosphin, is a colorless, poisonous gas, inflammable, odorous, resembles ammonia to some extent in its chemical properties, but is much weaker in alkalinity.

With oxygen:

P_2O_3 , phosphorus trioxid or phosphorous anhydrid.

P_2O_5 , phosphorus pentoxid or phosphoric anhydrid.

With oxygen and hydrogen:

Acids of phosphorus.

HPH_2O_2 , hypophosphorous acid.

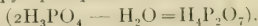
H_2PHO_3 , phosphorous acid.

H_3PO_4 , orthophosphoric acid.

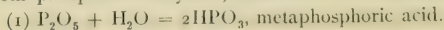
HPO_3 , metaphosphoric acid.



$\text{H}_4\text{P}_2\text{O}_7$, pyrophosphoric acid.



The important acids are the last three, all derived from phosphoric anhydrid, thus:



(2) $P_2O_5 + 2H_2O = H_4P_2O_7$, pyrophosphoric acid.

(3) $P_2O_5 + 3H_2O = 2H_3PO_4$, orthophosphoric acid.

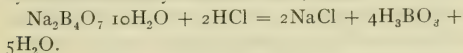
The *orthophosphoric acid* is the most important and is the one meant by "phosphoric acid." It is a liquid, the other two being solid. The *meta* acid is known as "glacial" phosphoric acid.

BORON.

Symbol, B. At. wt., 11. Valence, 3.

It is never found native in the free state, but may be prepared in two allotropic states, first as a greenish-brown powder; second, as a crystalline solid of varying colors, ranging from colorless to garnet.

Occurrence.—It is found in combination with calcium, magnesium and sodium as borates, the latter the most important, and known as *borax*, is found in India and California. As boric acid it is found in Tuscany. Boric acid is prepared from the borate by the action of hydrochloric acid, thus:



Boric acid separates in white, shining scales, is soluble in 25 parts of water and 3 parts boiling water, is a weak acid. A strip of turmeric paper dipped in a solution of boric acid turns cherry-red on drying.

Boric acid finds use as a mild antiseptic and detergent. Boric acid and its salts are poisonous to lower animals and plants and have produced serious conditions in human beings following its use too freely.

SILICON.

Symbol, Si. At. wt., 28. Valence, 2 and 4.

Occurrence.—Never found native, but may be prepared in three allotropic states—amorphous, graphitic and crystalline, somewhat resembling the three states of carbon. This element, next to oxygen, is the most abundant element in nature. It is found combined with oxygen as silica, SiO_2 , in quartz, sand, flint and many minerals. Clays are principally silicates of aluminum colored by iron or other mineral or vegetable matter. Neither the element nor its compounds are of much interest to the pharmaceutical student.

Compounds.—Silicic hydrid, SiH_4 , also bromid, SiBr_4 , and fluorid, SiF_4 , are known. SiO_2 , silicic oxid is the only oxid of this element, known as “silica,” a solid, tasteless, odorless, when freshly prepared, soluble in water, attacked only by hydrofluoric acid, and almost infusible by itself. Found in all granitic rocks which are composed of quartz, feldspar and mica. Quartz is almost pure silica, as also are sands and agates, the latter being a colloidal form deposited from silicious water. This silicious water is the chief agent in petrification. Silica forms the skeleton of certain invertebrate animals, is found in stems of plants, and hydrated it forms the opal.

When silica is fused with alkali carbonates or hydroxids, it forms silicates with these metals or a form of glass, the most important being the insoluble glass, silicates of sodium, potassium, lead or calcium or combinations of these with an excess of silica present.

Soluble glass is similarly made, but with an excess of the sodium or potassium. This product is also known as "water glass."

Silicic acid may be prepared by acting upon a dilute solution of an alkaline silicate with hydrochloric acid. It is only found in water solutions and is very unstable.

SELENIUM.—Symbol, Se. Valence, 2. At. wt., 78.87.

TELLURIUM.—Symbol, Te. Valence, 2. At. wt., 125.

These elements are called "rare" and are of little importance to the pharmaceutical student. They are found associated with sulfur and form acids similar to sulfurous and sulfuric acids.

CHAPTER VI.

WATER.

SYMBOL, H_2O . Mol. wt., 17.96.

History.—Until 1781 water was considered to be an element. At that time Cavendish proved its composition by synthesis. Priestley had also found that when hydrogen and oxygen were combined by explosion moisture was formed, but Cavendish first produced a sufficient amount of moisture to prove its identity.

In 1805, Humboldt and Guy Lussac determined the ratio of its constituents.

Occurrence.—Water is so widely distributed that it may be said to be almost universal.

It exists in three states of aggregation: Below $0^{\circ} C.$, it occurs as a solid; between $0^{\circ} C.$ and $100^{\circ} C.$, it takes the normal state of a liquid, and above $100^{\circ} C.$, it exists as a gas or vapor.

As gas we have water vapor as a constituent of air under normal conditions. The atmospheric moisture is produced by spontaneous evaporation, of both the land and water surfaces; from the formation of steam in manufacturing processes, respiration of animals and plants, etc.

Steam is gaseous water when first prepared, and at a temperature above $100^{\circ} C.$ it is colorless and invisible, but is easily reduced in temperature, and

what we ordinarily speak of as steam is a condensation of the vapor forming very fine drops of water. It is this partially or finely condensed moisture that we see in mists, fogs and clouds.

In the liquid condition, water is present in immense quantities in the ocean, lakes, rivers, smaller streams and as rain and as subterranean waters, soil moisture, etc. It also occurs, though hidden, as water of crystallization in many crystals, minerals, etc., and it is a large constituent of all the vegetable and animal organisms.

Thus, many vegetables are over four-fifths water, and over three-fourths the human body consists of water.

In the solid state, water occurs as snow, hail, and ice; the two former being modifications of the latter. Snow is, therefore, water congealed in the form of crystals. Hail is an accumulation of layers of ice formed to an irregular globe shape produced by natural precipitation in certain atmospheric currents and ice is also a crystalline congealed water form.

At a temperature of 0° C., water changes under normal conditions to a solid. As water cools it contracts steadily until a temperature of 4° C. is reached, when it begins to expand again until solidification occurs. Cooling then contracts the ice similarly to other solids. Ice, however, is lighter than water, and hence rises or forms at the surface of the water. If this were not true, bodies of water would freeze solid, even to the bottom, and lakes, streams, etc., would require great time and heat to

bring them to the liquid state again. Water at 4°C . is at its greatest density and at that temperature is taken as a standard of weight.

Water may be classified as follows:

Atmospheric	{	Rain.		
		Snow.		
		Hail, etc.		
Terrestrial	{	(a) Sweet	{	1. Springs.
				2. Ground.
				3. Well
				4. Pond or Lake.
				5. River.
	{	(b) Salt	{	1. Ocean.
				2. Inland Sea.
Mineral	{	1. Sulfur.		
		2. Saline.		
		3. Acidulous.		
		4. Chalybeate.		
		5. Alkaline.		
		6. Alum styptic.		
		7. Silicious.		
		8. Borax.		

Water when pure is a tasteless and odorless liquid. When seen in small quantities it is colorless, but in large masses it appears to be of a greenish or bluish color. This is largely due to the refraction of light rays, though it is thought that very finely divided suspended matter is also responsible for color in waters.

Water is a poor conductor of heat and is only very slightly compressible. It is the most important solvent and dissolves a larger number of substances than any other liquid. Owing to this property, no natural waters are found to be strictly pure, for even rain water contains foreign materials dissolved as the rain passes through the air.

Atmospheric waters. Rain water, as stated, is impure and may contain more or less of the following impurities: dust, germs, oxygen, nitrogen, carbon dioxid and ammonia from the air of which they are constituents. Nitric, nitrous and sulfuric acids organic substances, saline matter, ozone and hydrogen peroxid in very small amounts are also found.

In spite of this number of possible contaminating materials, rain water is the purest form of natural water and may contain, if collected in the country, an average of about 0.029 parts of foreign matter in 1000 parts of water. Collected in towns or cities, much larger quantities are present.

Rain water after reaching the earth becomes at once contaminated with various matters, depending upon the surface upon which it falls and the strata over or through which it may flow. It reappears as terrestrial water and will be so considered.

First, *spring water*. Is always chemically impure, the nature and quantity depending upon the locality and constituents of the soil, through which it passes. Generally clear, cool and sparkling and hence potable.

It usually contains (1) Chlorids, sulfates, bicar-

bonates of potassium, sodium, calcium and magnesium. (2) Nearly always silica and traces of aluminum and iron. (3) The atmospheric contamination material before mentioned. (4) Organic decomposition matter and bacteria usually harmless in nature.

A property more common to spring water than to other waters is hardness. This may be defined as that property of water which renders the formation of a lather with soap difficult. It is due largely to salts of lime, but also to salts of magnesium and iron. If these salts consist of carbonates which can be removed by boiling it, the hardness is known as "*Temporary*." If due to sulfates, however, boiling will not remove them, and it is then known as "*Permanent*" *Hardness*.

The incrustations forming in boilers, etc., are produced by the deposition of these mineral constituents. Temporary hardness crusts can be removed by ammonium chlorid, which converts the bicarbonates into readily soluble chlorids. Crusts produced by permanently hard waters are not affected by the ammonium chlorid. Numerous boiler compounds are on the market for this purpose, the best of which is trisodium phosphate, Na_3PO_4 .

Ground water is water held by the porous strata of the earth's surface as far as the first impervious layer, and has the same properties as the well waters.

Well Water.—Well waters are of three types as stated. Thus we have the open or dug well, the driven or drilled well and the artesian well. The first class is supplied with water from subterranean

springs or streams or from surface drainage. From the former source the water may contain the materials enumerated under spring water. The surface water supply may contain salts and nitrogenous matter from house drainage, also possible sewage from vaults and cesspools.

The much-applauded country well water may, unless much care is taken in its location, with relation to buildings, cesspools, vaults, etc., be a concentrated liquid full of infection and filth.

Driven wells come in for similar criticism, and much care should be exercised in selecting their location.

Artesian or deep strata wells are usually free from surface and organic impurities, but often are very heavily laden with mineral matter, and may thus be rendered unfit for potable purposes. Artesian wells, of course, can be obtained only in places where the strata so slope as to form a deep, impervious basin at the center of which the well is drilled.

Pond, Lake and River Waters.—These, generally speaking, are purer waters, naturally, than spring waters. Suspended matters are present in running water, but when the water comes to rest these matters are deposited as sediment and the water becomes clear.

Streams however, flowing through populous districts, often become contaminated with sewage, and when used as outlets for city refuse, sewage, manufacturing waste, etc., they become offensive and dangerous for potable purposes. These organic

matters, however, soon become oxidized with the oxygen held by the water itself, by the oxygen of the air and the effect of sunlight, and by action of bacteria present, and hence are rendered harmless. Flowing streams are supposed to purify themselves in from 8 to 12 miles, dependent upon the nature of their beds and the rate of flow. This is doubted by some authorities, however, and it is still an open question.

Ocean and Inland Sea Waters.—The water of the ocean contains a large amount of sodium chlorid and magnesium chlorid, some potassium, calcium and magnesium sulfates, sodium bromid and traces of other salts. The total average amounts to about 2138 grains (138 gms.) per gallon, of which about 80% is sodium chlorid (common salt). Inland seas contain much larger amounts—the Dead Sea about six times and Great Salt Lake seven times as much solids as the ocean. They also contain several salts not found in ocean water but due to the nature of the soil drained into them. Potassium chlorid and calcium chlorid are examples.

Mineral Waters are natural waters which contain unusually large quantities of some of the ordinary impurities or are characterized by unusual constituents; they are named according to their most prominent characteristics, thus:

(1) Sulfur water contains sulfur in form of hydrogen sulfid, metallic sulfids or even free sulfur. They usually also contain other salts. The odor of sulfuretted hydrogen is nearly always noticeable.

Examples: Harrowgate, of England, White Sulfur, of Virginia, and others throughout the United States.

(2) Salines, those having a salty taste, are of three classes: (1) Brines, in which sodium chlorid predominates, but usually also contain sodium bromid and iodid. Examples, salt wells of Michigan and springs at Syracuse, N. Y. (2) Bitter waters, containing calcium and magnesium chlorids, as St. Catherine Spring, Canada. (3) Purgative waters, containing magnesium or sodium sulfates, as Epsom Spring or Kissingen.

Acidulous waters contain sufficient free carbonic acid gas to produce effervescence, as appolinaris, selters, etc.

Chalybeates are those with iron present in medicinal quantities, usually in the form of bicarbonate or sulfate.

Alkaline waters are not alkaline when fresh, but if boiled the bicarbonates are changed to carbonates. Other salts generally present. Examples: Saratoga and Vichy waters.

Acid waters are those containing free acids, such as hydrochloric or sulfuric. Rio Vinaigre, of South America, contains both.

Alum waters contain alum, also, generally, sulfuric acid and iron. Rockbridge and Church Hill Alum Springs, both of Virginia, are examples.

Silicious waters are those containing considerable silica, usually hot springs. Geysers of Iceland are examples.

Borax waters contain borax in quantities profitable

to extract. Certain lakes of Thibet and California come under this class.

Artificial mineral waters if well made are of much medicinal value, but often nearly pure spring waters are sold as mineral waters and really have no such value.

Potable waters are those that are suitable for drinking purposes, and since these are of such great importance to man and since it has also been proven that waters are a fruitful source of supply of infectious diseases, it is essential that waters used for drinking purposes be as pure as possible. No natural waters are pure. Pure water may be obtained by distillation, by rejecting the first and last ten per cent. distilled, but even this is not the best potable water. For the best sustenance of the body a potable water should contain a trace of magnesium and calcium salts.

As a general thing, small amounts of mineral matters are not injurious to health; and organic matter in itself is not always certainly harmful, but it usually does show sewage or other contamination which might easily carry with it bacterial growths that could produce disease conditions. Chemical analysis, it is true, cannot prove bacteria present, but it can show the constants which, if large, go to indicate probable contamination and by this means lead to further investigation. Suspicious waters should always be refused and thorough examination of their source, chances of contamination, etc., made. Waters may be purified by numerous methods:

On the large scale by open sand filtration beds or by the later percolation spray system. In small household quantities by types of porous porcelain or charcoal filters, etc. Space will not allow of detailed discussion.

Usual types of waters called potable may be classified thus:

- | | | |
|------------|---|-----------------------------------|
| Safe | { | 1. Spring waters. |
| | | 2. Deep well waters. |
| | | 3. Mountain lake or river waters. |
| Suspicious | { | 1. Stored rain water. |
| | | 2. Surface water. |
| Dangerous | { | 1. River water with sewage. |
| | | 2. Shallow well water. |

Sewage is always dangerous, due to the liability of pathogenic bacteria being present.

Refuse from factories is usually not dangerous in running streams, for the poisonous materials either neutralize each other or are sufficiently diluted to render them harmless.

Metallic impurities usually are derived from pipes or tanks. Copper has been known to produce sickness. The most common form of sickness is lead poisoning. This is produced by the solvent action of the water, also of the dissolved carbon dioxide on the leaden pipes. Water that has stood for some hours in the leaden pipes should never be used for drinking.

Water may be examined for probable purity or contamination as follows: By noticing the taste,

odor, reaction, turbidity and color. It should be negative in all these respects.

Total residue is obtained by evaporating a known quantity to dryness. Dissolved solids, by filtering, evaporating and weighing. It may reach 30-50 grains per gallon safely.

Non-volatile residue is obtained by igniting the total residue. The loss on ignition shows organic constituents and should not be 50% of the total residue.

Hardness determined by Clark's test, which consists in using a standard soap solution to make a lather with the water. Small quantities are added with agitation until the lather persists for five minutes. A blank test must be carried out with distilled water. A water containing not over 50 parts per million of "hardness" is classed as a soft water, one with 150 parts is a hard water.

Chlorin is determined by the use of standard silver nitrate solution. One hundred cubic centimeters of the water is placed in a white porcelain dish, a few drops of potassium chromate indicator added and silver nitrate solution run in from a burette, drop by drop, till a slight red tint appears. If chlorin is present in very small amounts the water may be reduced to one-half its bulk by evaporation before titration. Too much dependence should not be placed upon amount of chlorin present, for larger amounts of organic matter may be present and very little chlorin be found. Also high chlorin present may be due to dissolved chlorids from the soil,

hence the characteristics of surroundings should be taken into account in the consideration of potability. Sewage generally contains about 11 parts per 100,000, and if conditions do not give reasons for high chlorine, over 5 parts per 100,000 may be considered suspicious of sewage contamination.

Sulfates are determined by precipitation as barium chlorid. Nitrites, by adding sodium sulfanilate and sulfuric acid, then naphthylamin. Nitrites will develop a pink color, the depth dependent upon the quantity of the nitrites present.

Nitrates, a simple qualitative test may be made, using diphenylamin in concentrated sulfuric acid. A deep blue indicates nitrates or nitrites. Quantitatively, nitrates may be tested by using sulfanilic acid and naphthylamin hydrochlorid.

Free ammonia is determined by use of Nessler's reagent in standard tubes for reading the color produced. Ammonia also exists combined and known as albuminoid ammonia. Water is first made alkaline with fixed alkali and distilled; the result is the amount of free ammonia. Permanganate of potassium is now added to the retort and further portions distilled over. The permanganate breaks down the albuminoids and ammonia is formed, which is distilled over and Nesslerized. A good water should not contain more than 0.1 parts of free ammonia or 0.15 of albuminoid ammonia in one million parts of water examined.

Organic matter is determined by the oxygen consuming power as measured by the amount

of potassium permanganate consumed in its oxidizing.

The mineral constituents, calcium, magnesium, etc., are readily determined by regular methods.

Bacteriologic examinations of water are very essential to a thorough understanding of its purity, and 1 c.c. of the water is placed in a shallow dish with 10 c.c. of sterilized beef extract as gelatin; covering carefully and allowing the bacteria to produce colonies. These colonies after a few days may be counted and each colony represents an individual original bacteria. The study of the variety of colonies may be carried as far as is desired.

Chemical analysis cannot always tell more than whether the water is contaminated or not, but with this as a guide we can carry our bacteriologic work as far as we please and prove the presence or absence of pathogenic bacteria.

In choosing potable waters from wells, springs, etc., care must be taken that cesspools, privies, manure piles and stable or kitchen refuse is not within 100 feet at least of the source of supply, and a study of the strata of the soil is valuable. If organic contamination is found, the only safe thing is to reject the water entirely. An understanding of conditions is quite necessary besides the chemical or bacteriologic examination.

CHAPTER VII.

THE ATMOSPHERE.

THIS name is applied to the gaseous mixture that envelops the earth. It is commonly called the air. The air is very elastic and hence is much denser near the earth and exerts at sea level a pressure of about fifteen pounds to the square inch. It becomes gradually lighter the farther away from the earth's surface and is thought to cease entirely at about twenty miles. One-half is contained in the first three miles.

The air consists of a mixture of gases, of which oxygen is the most important and nitrogen the most abundant. Lavoisier was first to definitely prove the presence of oxygen in the air, but Boyle, Priestley and Cavendish all had a part in its early investigation.

The air is proven to be a mixture, not a compound, by the facts that, first, an artificial air can be made by mixture only; secondly, the gases are not present in quantities represented by their atomic weights; thirdly, solvents of one gas dissolve it without reference to the others. It is a remarkably constant mixture, however, and hundreds of analyses showed an amount of oxygen varying only from 20.90% by volume to 20.99% by volume. One liter of air at normal conditions weighs 1.293 gms. One hundred cubic inches weigh 31 grains. It is

14.44 times as heavy as hydrogen. Gerecke was first to determine the weight of air.

The average composition in parts per 1000 volumes may be said to be:

Nitrogen,	779.00
Oxygen,	206.6
Aqueous vapor,	14.00
Carbon dioxid	0.34
Ammonia,	0.008
Ozone,	0.0015
Nitric acid,	0.0005
Argon, hydrogen peroxid, sul- furic acid, etc.,	mere traces.

The essential constituents are oxygen, nitrogen, carbon dioxid and water vapor, the others being in very small amounts or occur as impurities and hence require no special discussion.

Animal life is constantly taking up oxygen and giving off carbon dioxid. Vegetable life, however, takes up carbon dioxid and gives up oxygen, hence the balance is sustained. Air, as stated above always contains about such a ratio of oxygen and of nitrogen, and not much of the nitrogen of the air is consumed as such. Nitrates and nitrites occur occasionally due to direct union of nitrogen and oxygen, especially under influence of lightning flashes.

Water vapor or moisture in the air is very variable, the amount depending upon the temperature and locality. Saturated air is air holding all the vapor that it is capable of holding at a given temperature. Warm air will hold much more moisture

than cold air, thus air may be saturated at 25° C.; but if warmed to 50° C., seems quite dry, hence precautions should be taken to keep the air of living apartments properly moist, even if warm. If too dry, air is irritating to mucous membranes, but if too moist is oppressive by checking perspiration and raising body temperature. A very damp air also favors bacterial growth.

The dew point is known as the temperature at which the air begins to deposit its moisture. The percentage of humidity in meteorology means the ratio between the amount of moisture present and that necessary to saturate the air at the given temperature. One cubic foot of air at 25° C. will be saturated by about 10 grains of water vapor, but it seldom contains over about 70% of the amount required for saturation.

Carbon dioxid is present, due to combustion, respiration, etc., and in closely populated places the quantity increases largely. In poorly ventilated and crowded rooms it rises very high. In the country it is found only in about 4 parts per 10,000. Plants remove it from the air during the day, hence it is not so high in per cent. by day as by night.

Ammonia, nitrous and nitric acids, hydrogen peroxid, sulfuric acid, etc., are due to decomposition of organic nitrogenous matter, direct chemical reaction or direct union of the air constituents.

The air always contains some solid impurities, such as dust, clay and sand, some mineral salts, fragments of animal and vegetable tissues and refuse and

living bacterial products, moulds, yeast, other bacteria and their germs. This latter class of products produce moulds, decay, fermentations, and some even produce disease. Plant pollen often produces hay fever, and other foreign matter may produce irritation of mucous membranes, lungs, etc. In living apartments modern conveniences require the use of toilet equipment and these should be properly constructed in order to prevent contamination of the air we breathe.

Sewer gas contains methane and carbon dioxide largely, but also hydrogen, nitrogen, ammonia and acids and sulfur compounds, the latter usually causing the disagreeable odors noticed. It is not the gases that are productive of disease, but the bacteria which may be spread into the air. To prevent entrance of the foul odors and dangerous bacteria, proper plumbing should be installed. The soil-pipe and trap connections should open by a pipe through the roof of the house; the soil-pipe should be a 4-inch iron pipe and throughout its extent insure a flow of at least four and one-half feet per second. The traps should be siphon filling S-traps so as to be always automatic in filling, and the closets should be connected with the flush-box only—not with the large house tank, if such is used. A properly installed toilet will not give out any offensive odors and will be perfectly sanitary if properly cleansed and cared for.

Ground air, produced by decomposition of organic matters, is found in soil as far down as the

water level. In cellars, etc., this air sometimes collects and may be dangerous from its contaminating bacteria. The cellar floors and walls should be sealed by the use of pitch or other impervious materials.

The carbon dioxid of living-rooms is not always poisonous if it should come from other sources than respiration, organic decay, etc., but since this is the ordinary source in living apartments, proper means should be taken to remove the foul air and supply fresh, out-door air. Each human adult requires about 3000 feet of air per hour. This will require 1000 feet of air space, for air cannot well be changed oftener than three times an hour without undesirable air currents.

Modes of ventilation may be divided into (1) natural and (2) artificial. Natural methods depend upon (1) diffusion, which is of little service; (2) difference in density between warm and cold air: warm air rising and driving cold air in at a lower level; (3) the perflating and aspirating action of the wind. The fact that air currents will pass through small crevices in windows and walls produces a cross ventilation of a mild type. Care should be taken not to produce decided draughts, and numerous devices may be arranged.

The aspirating power is seen when wind blows over a chimney top: it displaces the air near the top, that lower down moves up to take its place, and thus the draught up the chimney is established. Heated air upon rising in the chimney serves to assist this power.

Fans are also used to force air out or into a room, but usually do little more than stir up the same air constantly. A reasonable amount of care in chimney construction and placing of windows usually produces good results; but if not, many commercial, scientifically built systems of ventilation may be obtained.

Sources of pollution of air we breath are: factories, putrefaction, ground air, respiration of animals and combustion in its multiple forms.

CHAPTER VIII.

ACIDS.

AN acid is usually defined as a substance containing hydrogen which is easily replaced by a metal. Acids are also defined as salts of hydrogen

Acids have some properties in common, as (1) all contain hydrogen, (2) when a metal and an acid are placed together, hydrogen is liberated and a salt formed; (3) they usually change vegetable colors; (4) they usually have a sour taste.

Acids are divided into classes according to the number of replaceable hydrogen atoms the molecule of the acid holds, thus:

Monobasic acids have but one hydrogen atom replaceable. Example, hydrochloric acid, HCl .

Dibasic, tribasic, tetrabasic, etc., contain, respectively, two, three and four replaceable hydrogens.

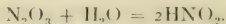
The basicity of acids allows the formation of normal and acid salts, a normal salt being produced when all available hydrogens are replaced; an acid salt being one in which not all of the replaceable hydrogen has been replaced. Acids are made up generally of hydrogen, a nonmetallic element, and may or may not contain oxygen. When it does not contain oxygen it is called a hydracid, and has the prefix "hydro" and the termination "ic"; thus, HCl = *hydrochloric acid*. The class is comparatively small. When oxygen is present they are known as the

oxacids. The best known, normal, or most important acid is generally without prefix, but ends in "ic," as sulfuric acid, H_2SO_4 . If another contains less oxygen, this has the suffix "ous." Some elements form acids with still less oxygen. The prefix "hypo" (meaning below) is used, and also the ending "ous." If the same element forms an acid of greater oxygen content than the "ic" acid, the prefix "per" (meaning more) is applied and also retains the suffix "ic." Acids may be solid, liquid or gaseous, or solutions of each.

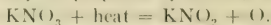
They occur both naturally weak or strong in acid properties, and both concentrated and dilute dependent upon their purity and dilution with a solvent, usually water. Each acid in addition to the general acid properties also has its own special properties differing from the others, and these will be taken up under the acids themselves. According to their basicity, the following list of important acids is arranged.

Nitrous Acid, $\text{HNO}_2 = \text{H} - \text{O} - \text{N} = \text{O}$.

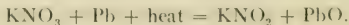
Not known in the pure state, but it exists in solution, and a number of its salts are in common use. It may be prepared by passing nitrous anhydrid (trioxid) into water.



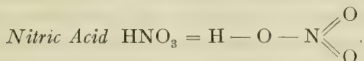
The salts may be prepared by heating nitrates.



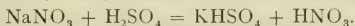
Usually some readily oxidizable substance is added, thus:



In nature, the nitrites are produced by the oxidation of nitrogenous organic matter; this occurs in water and soils.

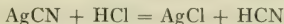


Known as aqua fortis (strong water). A colorless liquid, pungent, very acid taste and gives off red fumes when heated. Very corrosive, staining the skin yellow, and forms picric acid applied to the skin. Prepared by acting on a nitrate with sulfuric acid, thus:



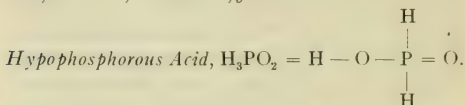
Its specific gravity is 1.52, strength 68% when pure, boils at 86° C. and solidifies at 40° C. When heated it is decomposed into nitrogen tetroxid, water and oxygen. It gives up part of its oxygen so readily that it acts as a strong oxidizing agent. It acts readily upon most metals, producing salts, and upon nonmetals, oxidizing them. All nitrates are soluble in water. Aqua regia—Nitrohydrochloric acid is prepared by mixing four parts of hydrochloric and one part nitric acid, and has the property of dissolving gold, platinum and other refractory metals. Fuming nitric acid is a reddish-brown liquid containing dissolved nitrogen trioxid or tetroxid, and is a powerful oxidizing agent.

Hydrocyanic acid, $\text{HCN} = \text{H} - \text{HCN} = \text{H} - \text{C} \equiv \text{N}$, called *prussic acid*, is best prepared by decomposing metallic cyanids with hydrochloric acid, thus:

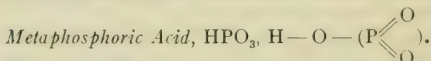


It boils at 26.5° C., is soluble in water. Is a colorless

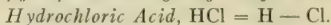
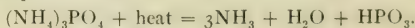
liquid with very characteristic odor and taste, familiar to us as the odor of oil of bitter almonds, which contains considerable of the acid. It is very poisonous, and since it volatilizes very readily from solution or salt compounds of hydrocyanic acid, should be handled very carefully. The dilute hydrocyanic acid, U. S. P., contains 2% of HCN.



A syrupy, colorless, strongly acid liquid, unstable, readily oxidizing to phosphorous and phosphoric acids. The acid is 30% strong, and is not largely used, but the salts, called hypophosphites, are of considerable value. Acid hypophosphorous dilute is a 10% solution of acid, it is a colorless, odorless liquid, miscible with water. It is changed by high heat to phosphoric acid and phosphin. May be tested by silver nitrate, which it reduces to metallic silver.



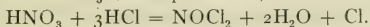
Called glacial phosphoric acid, and occurs as a white, glassy, colorless solid. Forms salts known as metaphosphates, as sodium metaphosphate, NaPO_3 . Usually the acid is prepared by heating ammonium phosphate thus:



Hydrogen chlorid, muriatic acid "spirit of salt."

Occurs but little in nature, but is found in volcanic gases and in gastric juices of mammals. It is a colorless, invisible gas, with a pungent, penetrating, irritant odor, a sharp, acid taste and acid reaction. It is irrespirable and does not burn or support combustion; very soluble in water, and its solution forms the customary acid of commerce. One volume of water contains 450 volumes of the gas. It has a specific gravity of 1.21, and contains about 32% of the acid. The pure gaseous acid may be reduced to a liquid at 10° C. with 40 atmospheres of pressure. The U. S. P. acid is a fuming liquid of 31.9% strength; specific gravity at 25° C. is 1.158. Dilute hydrochloric acid U. S. P. should contain 10% of acid; has a specific gravity of 1.050 at 15° C.

Nitromuriatic Acid U. S. P. (see Aqua Regia), 180 parts HNO_3 + 820 parts HCl , reacts thus:



Derives the name aqua regia because it will dissolve gold, the king of metals.

Hypochlorous acid, $\text{HClO} = \text{H}-\text{O}-\text{Cl}.$

Chlorous acid, $\text{HClO}_2 = \text{H}-\text{O}-\text{O}-\text{Cl}.$

Chloric acid, $\text{HClO}_3 = \text{H}-\text{O}-(\text{O}-\text{O}-\text{Cl}).$

Perchloric acid, $\text{HClO}_4 = \text{H}-\text{O}-(\text{O}-\text{O}-\text{O}-\text{Cl}).$

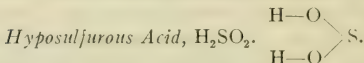
Bromin and iodine form similar series to the above, but all are of insufficient importance to consider individually. (See Bromine and Iodine.) Hydrofluoric acid is the only acid of fluorine of any importance and this is little used in medicine. (See Fluorine.)

DIBASIC ACIDS

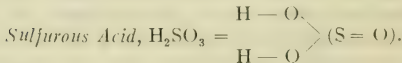
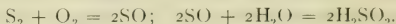
(Normal and Acid Salts.)

Hydrosulphuric $\text{H}_2\text{S} = \text{H} - \text{S} - \text{H}$.

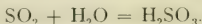
Hydrogen sulfid, sulfuretted hydrogen, prepared by action of sulfuric acid and ferrous sulfid.



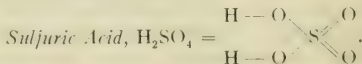
Prepared by burning sulfur with partial air supply, and passing the gas into water. Thus:



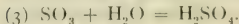
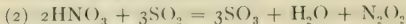
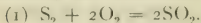
Sulfur burned with oxygen gives sulfurous anhydrid, SO_2 , this dissolved in water gives.



Its salts are called sulfites and are of some importance in medicine for their antiseptic properties and in the arts as reducing agents.



Oil of vitriol. Hydrogen sulfate. Obtained from pyrites, FeS , by heating, forming sulfurous anhydrid, oxidizing and hydrating this to sulfuric acid.



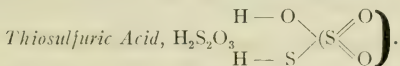
Chamber acid has a specific gravity of 1.55.

Pan acid has a specific gravity of 1.74 = 78%.

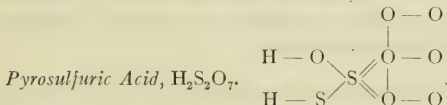
Concentrated acid has a specific gravity of 1.83 = 92.5 %.

It is an oily, heavy, corrosive acid, colorless if pure, colored brown if impure. Dilute sulfuric acid U. S. P. contains 10% sulfuric acid.

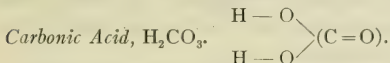
Aromatic sulfuric acid contains 18.5% absolute or 20% U. S. P. sulfuric acid, combined with alcohol and aromatic tinctures.



Not found in the acid form, but the salts are used.



Nord Hausen sulfuric acid, a heavy, brown, oily liquid, thought to be a solution of SO_3 in H_2SO_4 .



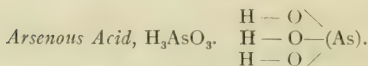
Important only for its salts, the carbonates and bicarbonates. Unstable, feeble acid. Easily decomposed, forming carbon dioxid, CO_2 , and water, H_2O .



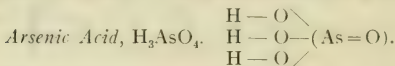
A colorless liquid, easily oxidized, its salts are known as phosphites.

TRIBASIC ACIDS.

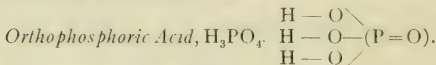
(These Form Three Types of Salts—Normal,
Acid and Double.)



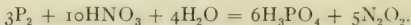
Prepared by roasting arsenic ores, which produces the arsenous oxid, AsO_3 , which is the most important arsenic compound. This oxid, $\text{As}_2\text{O}_3 + \text{water}$
 $3\text{H}_2\text{O} = 2\text{H}_3\text{AsO}_3$. The salts are known as arsenites.



Usually prepared by oxidizing arsenous acid by nitric acid and evaporating the solution. The salts are known as arsenates.



Phosphoric acid ordinary is the most important acid of phosphorus. Prepared by boiling phosphorus with dilute nitric acid and evaporating to a syrupy consistency.

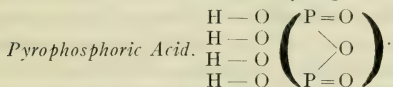


It is colorless, odorless, strongly acid liquid and contains 85% of absolute phosphoric acid. Is miscible with water and alcohol in all proportions. It has a specific gravity of 1.71 at 15° C. Heated to 200° C., it loses water and changes to pyrophosphoric acid, $\text{H}_2\text{P}_2\text{O}_7$. At still higher temperatures, it forms metaphosphoric acid, HPO_3 . Dilute phosphoric acid

U. S. P. contains 10% of acid, and has a specific gravity of 1.057 at 15° C.

TETRABASIC ACIDS.

(Those Having Power of Forming Four Classes of Salts or With Four Available Hydrogens.)



Forms salts known as pyrophosphates; sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$.

CHAPTER IX.

METALS.

OVER fifty metals are included in the ordinary classification, but the number is being constantly increased by new discoveries, and older ones are frequently separated into simpler ones. Of these only twenty-seven are considered as common metals, the remainder being known as rare metals. This is not strictly true, but only those that are of pharmaceutic importance will be considered in detail, and these number only about twenty-five.

The classification and order of study will be that commonly employed in qualitative analysis in order to teach both the general properties and the methods of separation at the same time. Classifications in relation to atomic weight and valence are given on pages 78, 173, 178.

There are certain characteristic properties possessed by all metals:

1. Metallic luster, quite distinctive.
2. Good conductors of heat and electricity, and often used for such purposes.
3. All solids at ordinary temperature except mercury, which is the only liquid metal.
4. Nearly all electro-positive.
5. Color variable within limits of shades of white and gray, except copper and gold.

6. Weight, heavier than water, with the exception of lithium, potassium and sodium, which are lighter than water.

7. Malleability marked, gold being exceedingly malleable and sodium the least so.

8. Ductility, tenacity or cohesion, these varying from the greatest tenacity of silver and iron to lead, the least tenacious.

9. Fusibility, nonvolatility at ordinary temperature and insolubility in ordinary solvents (water, alcohol, ether).

The metals occur in varying abundance in ores, rocks and soils throughout the earth's crust and often as pure metal in the so-called pockets and veins.

The methods of extraction are variable and will be individually discussed. The following classification will be followed for the more common metals, and the rare metals will be discussed in a chapter by themselves.

GROUP I. Hydrochloric Acid Group	GROUP II. Hydrogen Sulfid Group 1st Div.	GROUP III. Sulfid Group 2d Div.	GROUP IV. Ammonium Sulfid Group. 1st Div.	GROUP V. Sulfid Group. 2d Div.	GROUP VI. Carbonate Group	GROUP VII. Alkaline Group	GROUP VIII. Rare Metals
I. Mercury Hg (Mercurous) II. Lead Pb III. Silver Ag Precipitated by HCl as in- soluble chlorids.	I. Arsenic As II. Antimony Sb III. Tin Sn	I. Bismuth Bi II. Copper Cu III. Mercury HgII IV. Cadmium Cd	I. Zinc Zn II. Cobalt Co III. Nickel Ni IV. Manganese Mn	I. Aluminum Al II. Chromium Cr III. Iron Fe	I. Calcium Ca II. Strontium Sr III. Barium Ba IV. Magnesium Mg Precipitated by soluble carbonates.	I. Lithium Li II. Sodium Na III. Potassium K IV. Ammonium NH ₄ No precipitate Individual tests.	Group I. Thallium Tungsten II. Ruthenium Rhodium Radium Osmium Iridium Tellurium Selenium Molybdenum III. Baryllum Zirconium Thorium Cerium Scandium Yttrium Lanthanum Ytterbium Titanium Tantalum Niobium Uranium Indium Thallium Vanadium IV. V. Rubidium Cesium
	Entire group ppt. by H ₂ S. 1st Div. Soluble in ammonium polysulfid.	2d Div. Insoluble in ammonium polysulfid.	Entire group precipitated by ammonium sulfid. 1st Div. Precipitated as sulfids in presence of NH ₄ OH and NH ₄ Cl. 2d Div. Not precipitat- ed in presence of NH ₄ OH and NH ₄ Cl as sulfids, but as hydrates by NH ₄ OH alone and so separated.				

CHAPTER X.

SILVER, LEAD AND MERCURY.

THE hydrochloric acid group, is so called on account of their precipitating from their solutions by the use of hydrochloric acid or soluble chlorids, forming insoluble chlorids with these metals.

This group is also considered first because of the importance of the compounds and the fact that they are fewer in number and simpler in their composition. The metals included are mercury, Hg, which exists in this group in the univalent or monad state, lead, Pb, and silver, Ag. The salts or compounds of the dyad mercury, will be discussed in Chapter XII.

MERCURY, Hg. Hydrargyrum U. S. P. At. Wt., 198.5 (200). Sp. gr., 13.5. Valence, 1 and 2. Common name, quicksilver.

Source.—Occurs in nature chiefly as cinnabar, HgS, mercuric sulfid; rarely, as globules of the metal enclosed in rocks. Obtained chiefly from Spain, but also in Peru, Mexico and Japan.

Preparation.—From cinnabar by roasting, the sulfur uniting with oxygen to form gaseous sulfur dioxid and escaping while the mercury distills. Thus, $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$.

Properties.—A silver-white, lustrous metal, liquid at ordinary temperature, congealing at 38.8°C

boils at 360° and very slightly volatile at ordinary temperature. It has the same atomic weight and vapor density, hence its molecule consists of one atom only. If pure, it is unchanged at ordinary temperature, but above 300° it becomes coated with a film of mercuric oxid readily acted on by nitric acid but more difficultly by sulfuric and hydrochloric in the cold. Pure mercury poured on glass or paper does not adhere or form tails to the drops, but retains its spherical shape. It forms two series of compounds the mercurous and mercuric. The former are less stable, contain a larger percentage of the metal, are less soluble and consequently less poisonous.

Toxicology.—Metallic mercury is not poisonous, but when it or its salts become soluble, their poisonous nature is very pronounced. Children tolerate mercurials much better than adults. Treatment of poisoning should consist of albumen, as milk or eggs, and prompt emesis.

Tests.—Mercurial compounds in solution are readily detected by immersing a strip of bright copper foil in the solution in the presence of free hydrochloric acid. A white-silvery film of copper amalgam quickly forms. Solutions also give a black precipitate with hydrogen sulfid and a white precipitate with hydrochloric acid if in the mercurous state.

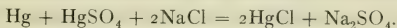
Uses.—Mercury metal is used in many amalgams, since it forms amalgams with nearly all metals. Tin amalgam is used for coating mirrors. The metal as such is largely used for thermometers, barometers, thermostats and other instruments, and it enters

into five official preparations, viz.: Emplastrum hydrargyri, U. S. P., 30%; Massa hydrargyri, U. S. P., 33%; Hydrargyrum cum creta, U. S. P., 38%; Unguentum hydrargyri, U. S. P., 50%, and Ung. hydrargyri dilutum, U. S. P., 33.3%.

Compounds.—It may be remembered that all the official compounds of mercury are required to be 99½% pure, except hydrargyrum ammoniatum, which is 78%. The mercurous salts of the U. S. P. are but two in number—for instance, the chlorid, HgCl, and iodid, HgI. Other salts of some importance, however, are the oxid, nitrate and sulfate.

I. *Mercurous chlorid* (Hydrargyri chloridum mite U. S. P.), HgCl, calomel, *mild chlorid of mercury*, proto chlorid, subchlorid, submuriate of mercury, or, mercurius dulcis.

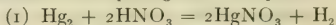
A heavy, white, impalpable powder, insoluble, volatile, prepared usually by subliming mercury, mercury sulfate and sodium chlorid, and washing out the corrosive chlorid that also forms.



It may be also prepared by heating mercury with mercuric chlorid: $\text{Hg} + \text{HgCl}_2 = 2\text{HgCl}$; by mixing solutions of mercurous nitrate and sodium chlorid: $\text{Hg}(\text{NO}_3) + \text{NaCl} = \text{NaNO}_3 + \text{HgCl}$; also by a solution of mercurous nitrate and mercuric chlorid, $\text{Hg}_2(\text{NO}_3)_2 + \text{HgCl}_2 = 2\text{HgCl} + \text{Hg}(\text{NO}_3)_2$. It is used medicinally as a laxative and alterative.

Yellow mercurous iodid (Hydrargyri iodidum flavum U. S. P.), HgI, protoiodid, yellow iodid, green iodid, hydrargyri iodidum, viride, U. S. P., '80. A

yellowish-green, insoluble salt prepared by dissolving mercury in dilute nitric acid to form mercurous nitrate and decomposing this with potassium iodid:



Used as an alterative.

Mercurous oxid, Hg_2O , protoxid, or black oxid, prepared by interaction of sodium hydrate and mercurous nitrate. $\text{Hg}_2(\text{NO}_3)_2 + 2\text{NaOH} = \text{Hg}_2\text{O} + 2\text{NaNO}_3 + \text{H}_2\text{O}$. A brownish-black, heavy, tasteless, insoluble powder; unstable, sunlight converting it into mercuric oxid and mercury. It is the essential ingredient of *lotio nigra*, or black wash of the N. F., made by adding calomel to lime-water, $2\text{HgCl} + \text{Ca}(\text{OH})_2 = \text{Hg}_2\text{O} + \text{CaCl}_2 + \text{H}_2\text{O}$.

Mercurous nitrate, HgNO_3 , white or colorless, prismatic and very unstable, efflorescent, crystals prepared by action of dilute nitric acid on mercury. $6\text{Hg} + 8\text{HNO}_3 = 3\text{Hg}_2(\text{NO}_3)_2 + \text{N}_2\text{O}_2 + 4\text{H}_2\text{O}$. Mercurous sulfate, Hg_2SO_4 , a white, crystalline salt, easily decomposed to the basic salt, prepared by action of sulfuric acid on an excess of mercury, is of very little value. For discussion of mercuric compounds, see Chapter XII.

LEAD, *Plumbum*, Pb, 205. Sp. gr., 11.4. Melting point, 325° . Sometimes found free, but commercially in abundant ores chiefly as sulfid, galena, PbS , and as carbonate, *cerusite*, PbCO_3 . The ores usually contain some silver, which is removed by crystallizing and cupelling. The lead is obtained by continued roasting of the ores.

Properties.—A soft metal, bluish-white, brilliant silvery luster on fresh surfaces, but quickly tarnished. It is malleable and pliable, but not ductile or tenacious. Conducts heat well, electricity poorly, melts at 325° and volatilizes at a white heat. It is precipitated from its solutions by zinc, tin and iron, acted upon slowly by most acids, but freely by nitric acid. In presence of air, water dissolves lead by forming the hydroxid. Nitrates and nitrites increase, and carbonates, chlorids and sulfates decrease this solubility. These facts are important because potable waters are so commonly conducted through lead pipes.

Uses.—The commercial uses of the metal are well known. It also forms a number of useful alloys: with tin it forms solder, fusible at 186° ; with zinc it forms Babbitt metal, and with antimony forms type-metal and is an ingredient of types of glass known as flint glass. The greatest consumption of lead, outside of its mechanical uses in pipes, sheetings, etc., is probably as a paint pigment in the form of basic lead carbonate, or white lead, $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, even yet largely manufactured by the old Dutch method, dependent upon the corrosion of the lead by acetic acid in the presence of carbon dioxid and moist air. Other methods have been devised, but the Dutch method seems to give the greatest satisfaction.

Toxicology.—All soluble lead compounds and those that are rendered soluble in digestive fluids or otherwise in the animal economy are quite poisonous.

The chronic form of poisoning, known as painters' colic, is very common, due to contact with the compounds of lead in painting, etc.

The acute conditions of poisoning are quite rare and seldom fatal and usually produced by a large single dose of such salts as acetate or carbonate. When such a case occurs, magnesium sulfate should be at once administered, as it produces an insoluble sulfate with the lead. Emesis should be induced.

Compounds.—*Lead acetate*, (Plumbi acetas U.S.P.), $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$. sugar of lead, sal saturni, colorless, shining, transparent, prisms or plates, heavy crystalline masses or granules, with a faint acetous odor, sweetish, astringent, metallic taste; efflorescent; absorbs carbon dioxid from the air. Soluble in two parts of water. Incompatible with very many substances, such as alkali salts, organic salts and soluble chlorids and sulfates. May be made by dissolving lead oxid in acetic acid and crystallizing. $\text{PbO} + 2\text{C}_2\text{H}_4\text{O}_2 = \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$. Used medicinally as an external astringent. Enters into emplastrum plumbi, ung. diachylon, 50%; liq. plumbi subacetate, 25%; liq. plumbi subacetatis dilutus, 1%, and ceratum plumbi subacetatis—20%. *Lead iodid*, Plumbi iodidum, PbI_2 , precipitated from lead solutions by potassium iodid. Should be preserved in well-stoppered bottles away from light. A heavy, bright-yellow powder, odorless, tasteless and slightly soluble in water. (1-1300) 99% pure. Used medicinally as a sorbefacient. The ointment of lead iodid, 10%, was formerly official.

Lead nitrate (Plumbi nitras), $\text{Pb}(\text{NO}_3)_2$, 99.5% pure. Prepared by dissolving lead or its oxids in excess of nitric acid. $\text{PbO} + 2\text{HNO}_3 = \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$. Colorless, octahedral crystals, sometimes transparent, often nearly opaque. Odorless, sweetish, astringent, metallic taste. Soluble in less than two parts of water. It is used as a caustic applied as a powder; its solution is used as a disinfectant.

Lead oxid (Plumbi oxidum), PbO , 96% pure, (litharge). Prepared by heating metallic lead, its carbonate or nitrate with access of air, obtained largely as a by-product in silver extraction. A heavy, yellow or reddish-yellow powder, odorless and tasteless. Insoluble in ordinary solvents, readily so in acetic and nitric acids. Used in the preparation of various lead salts, solution of lead subacetate and formerly in preparing lead plaster. Other oxids of lead: dioxid, PbO_2 , plumboso-plumbic oxid, or red lead, Pb_3O_4 , and plumbic suboxid, Pb_2O . None are of much importance. Lead chromate, PbCrO_4 , "chrome yellow," is much used as a pigment. Lead sulfid and lead carbonate have been mentioned.

SILVER, Ag., Argentum, 108. Valence, 1.

Occurrence.—Occurs native to a small extent, but principally as ores in combination with chlorin, bromin, sulfur, etc. Associated with lead, copper, gold, etc. Found principally in western United States, Mexico, Hungary and Saxony.

Preparation.—The ore is roasted with sodium chlorid forming silver chlorid, and this is decomposed by iron scraps. Metallic mercury is added,

forms an amalgam with the silver, and the mercury is distilled from it. Different ores require individual treatment, however, and works on metallurgy should be consulted for full details of extraction.

Properties.—It is a white, lustrous metal, permanent in the air, very malleable, tenacious, and ductile. An excellent conductor of heat and electricity, feebly attacked by most acids, but freely by nitric acid. Specific gravity, 10.5; melting-point, 1040°.

Uses.—Seldom used by itself, on account of its softness, but usually combined with copper to harden it. Used much in art work, cutlery and as a coin medium, ornaments, etc. Coin silver contains 10% copper in the coins of the United States, France, Germany and Austria. British coin silver contains 7.5% copper. In pharmacy and medicine silver is used for surgical instrument plating and in the preparation of silver salts.

Compounds.—*Silver cyanid* (Argenti cyanidum U. S. P.), AgCn ; purity, 99.5%, equivalent to 80.5% metallic silver. Prepared by passing hydrocyanic acid through solution of silver nitrate or adding a soluble cyanid to the same.

Properties.—A white, permanent powder, odorless and tasteless. Insoluble in ordinary solvents, but soluble in ammonia water and potassium cyanid solution. In solution with the latter it is used in electro-plating. Used for the extemporaneous preparation of dilute hydrocyanic acid, 2%.

Silver nitrate (Argenti nitras U. S. P.), AgNO_3 ; purity, 99.9%. Should be kept protected from light.

Preparation.—Made by dissolving silver in diluted nitric acid.

Properties.—Colorless, transparent, tabular rhombic crystals reduced to grayish-black by light or organic matter. Odorless with a strongly metallic and caustic taste. Soluble in 0.54 parts of water, 24 parts of alcohol. Incompatible with alkalies, most acids and organic matter. Melts at about 200° to a faintly yellow liquid. When so fused and cooled in moulds, it forms the official argenti nitras fusus U. S. P., known as lunar caustic and “lapis infernalis.” When one part silver nitrate and two parts potassium nitrate are fused together and moulded, it is called argenti nitras dilutus U. S. P., or mitigated caustic. The salt is useful as an antiseptic, astringent and caustic. It also finds use in photography, in the manufacture of hair dyes, indelible inks and in silvering mirrors, etc. It is poisonous, sodium chlorid being the best antidote. Silver stains on the skin may be removed by solution of potassium cyanid, sodium thiosulfate or ammonia water.

Silver oxid (Argenti oxidum), Ag_2O ; purity, 99.8%; equivalent to 92.9% silver. Easily reduced by light organic matter and ammonia.

Properties.—A heavy, dark-brownish to black powder, odorless, with metallic taste. Slightly soluble in water. Decomposed at 300° . Feebly astringent.

The chlorid, bromid and iodid of silver are very similar, insoluble, easily reduced and find their

greatest use in photography, which depends upon the ready reduction of these salts when exposed to light.

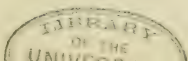
Toxicology.—Poisoning by silver salts is quite rare, sodium chlorid or other soluble chlorids being the antidotes.

CHAPTER XI.

ARSENIC, ANTIMONY, TIN.

THIS group is, as a whole, known as the hydrogen sulfid group, because the metals included in the group will be precipitated from acid solution by the general group reagent, hydrogen sulfid, H_2S . After separating the metals of Group I by hydrochloric acid, the residual solution is treated with a current of hydrogen sulfid gas. The metals are precipitated as sulfids. We further divide this group into two divisions. Those metallic sulfids previously formed that are soluble in ammonium sulfid, viz.: arsenic, antimony and tin; and those insoluble in ammonium sulfid, viz.: bismuth, copper, cadmium, mercuric mercury and lead. The former group is the subject of this chapter. The medicinal uses of these metals are but few and very few of the salts are official. Arsenic is the most valuable of the three, medicinally.

ARSENIC, Arsenum, As, 74.4. Mol. wt., 299. Sp. gr., 5.7. Arsenic is found free in nature, but usually combined with sulfur or oxygen. Its principal ores are orpiment, As_2S_3 , realgar, As_2S_2 , and iron arseno-sulfid, $FeAsS$, also called "mispickel" or arsenical pyrites. It is widely scattered, though in minute quantities, throughout inorganic and many organic compounds. It is commonly present in



iron pyrites and through this channel finds its way as an impurity into sulfuric acid, which is prepared from pyrites.

Preparation.—Arsenic is prepared from pyrites by roasting to volatilize the arsenic which afterwards is purified by distillation.

Properties.—Arsenic in many ways resembles a true metal, but it also has the properties of a non-metal, and since it possesses both the properties, it is often styled a metalloid (metal-like) element. It occurs both as amorphous substance and in irregular rhombohedral crystals. It volatilizes above 100° C. and at 180° C. is vaporized rapidly without melting. When so heated in presence of air, it unites with oxygen, producing grayish fumes which possess a garlicky odor. It burns with a bluish flame, which results in the production of an oxid. This oxid, chemically a trioxid, has the formula of As_2O_3 . Arsenic finds uses in the hardening of shot, in pyrotechny, in the manufacture of paint pigments and is alloyed with iron and copper to increase their degree of brilliancy when polished. It is also used to produce many of the vermin poisons in agriculture.

Compounds.—Arsenic forms two classes of compounds, the “ic” and the “ous.” In the “ous” condition, it acts as a trivalent. In the “ic” as a pentavalent. Arsenic oxid, As_2O_5 , when dissolved in water forms arsenic acid, which has the formula H_3AsO_4 , and which forms salts called arsenates. The arsenic oxid is less poisonous than the arsenous oxid. This latter oxid, official in the U. S. P. under

the title of arseni-trioxidum, As_2O_3 , commonly called arsenic, white arsenic, arsenic trioxid or ratsbane, is a white, gritty, crystalline powder, which, fused in sealed glass tubes, produces a vitreous mass gradually becoming opaque. It is slightly soluble in water, producing arsenous acid, H_3AsO_3 , which forms unstable salts known as arsenites. The official article should be not less than 99.8% pure. The glassy variety changes by exposure to moist air to the opaque variety which is more readily soluble. Medicinally, arsenic is used as a caustic, tonic and alterative, thought to be specific in various skin diseases. It enters into the solution of arsenous acid (liquor acidi arsenosi, 1%), the Donovan solution (liquor arseni et hydrargyri iodidi, 1% each), into the solution of sodium arsenate (liquor sodii arsenatis, 1%), and into the Fowler's solution (liquor potassii arsenitis, 1%). Of the chemical compounds of arsenic official we find the iodid (arseni iodidum), AsI_3 , which represents 16.3% of metallic arsenic and 82.7% of iodine. It is made by the direct union of the elements. It occurs in orange-red, crystalline odorless powder, soluble, but partly decomposed in 12 parts of water, readily soluble in ether and chloroform. It should be protected from heat and light. The iodid is incompatible with most metallic salts, except the alkali metals. It is easily reduced or oxidized. Medicinally, the salt is used as an alterative. Arsenic forms similar compounds with the other halogen elements. Three sulfids of arsenic are known: arsenous sulfid, As_2S_3 , the disulfid,

As_2S_2 , and the pentasulfid, As_2S_5 . Cupric arsenite $\text{Cu}_3(\text{AsO}_3)_2$, is called Scheele's green. Paris green, or Schweinfurt's green, is a variable mixture of copper, acetate and arsenite, usually supposed to be cupric aceto-arsenite, made by boiling arsenous oxid in a solution of copper acetate and the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{Cu}(\text{AsO}_2)_2$, has been ascribed to it. Both the greens are used as pigments in wall paper printing and the detached particles therefrom have frequently produced symptoms of chronic arsenical poisoning. The detection of arsenic in wall paper is frequently called for and the pharmacists should be ready to perform the same.

Toxicology.—Arsenic is an important poison and from the time of its discovery has been used for criminal purposes. All soluble compounds of arsenic are poisonous, the poison usually enters the system by the mouth, but it may be absorbed by the skin, membranes or by breathing. It permeates the entire body, but deposits more specifically in the liver. It is excreted both by the feces and by urine. In case of poisoning with arsenic, the stomach-tube is the first indication, emetics should be promptly administered. The chemical antidote is the ferric hydroxid or better the official ferric hydroxid with magnesia (ferri hydroxidum cum magnesii oxido), commonly known as the "arsenic antidote." This antidote is most admirable in its action: thus, the magnesium oxid which it contains neutralizes the acid of the gastric contents, producing neutral salt and thus preventing the solution of arsenic therein.

Dialysed iron is another form of iron found very effective, in both cases the iron combining with the arsenic and forming an insoluble ferric arsenate.

Tests.—Numerous tests for the detection of arsenic are available, but no single test should be regarded as conclusive. *Marsh's test* is possibly the most important, though in presence of organic matter it is not positive. This is conducted as follows: introduce into a flask some arsenic-free zinc (U. S. P. reagent) cover it with dilute sulfuric acid, close the flask with a stopper, perforated and supplied with a safety tube and provided with another tube turned at right angles horizontally drawn out to a fine point. The metallic zinc decomposes the acid and generates hydrogen, which in turn should be allowed at least fifteen minutes to drive out all the air from the container. The arsenical solution should next be introduced through the safety tube, the gas at the open end of the tube should next be lighted and a piece of cold porcelain dish (a porcelain crucible lid will do) held against the flame; if no black stain appears, arsenic and antimony are not present. If a brownish-black spot is deposited, which when treated with a few drops of a solution of a hypochlorite dissolves, it indicates arsenic. If it does not dissolve, antimony is indicated. This test depends on the formation of arsin gas, AsH_3 , the product of the action of nascent hydrogen on arsenic in acid solutions.

Fleitmann's test depends on dropping a few pieces of metallic zinc or aluminum in a solution of potassium hydroxid, which contains a small quantity of

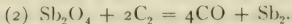
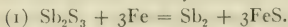
the arsenical solution. The test-tube is covered with a piece of filter paper which has previously been moistened with a solution of AgNO_3 . The arsingas which is evolved acts upon the silver nitrate reducing it to metallic silver which produces a dark stain upon the paper. This test is important and valuable in that it differentiates arsenic from antimony (stibine not being evolved).

Guttzeit's test depends upon the reduction of lead acetate by arsin, and *Reinsch's test* depends upon the reducing powers of copper on arsenical compounds.

ANTIMONY, Stibium, Sb, 119.3. Sp. gr., 6.7. Melting-point, 450 C.

Occurrence.—Antimony occurs native, scattered widely, but only in minute particles. It is found in combination as an oxide, Sb_2O_3 , commonly known as "antimony bloom" or white antimony, and as antimony ochre, AsSb_2O_4 . In combination with sulfur, it occurs as stibnite, Sb_2S_3 , which is its most important ore and commercial source. It is also found combined with iron, copper, lead and other sulfides.

Preparation.—Antimony is obtained from the sulfides by heating with scrap iron in carbon crucibles or by roasting the ore with half its weight of charcoal. The two methods of extracting the metal from the ores will best be seen by the following two equations:



Properties.—Antimony is a bright, silver-white,

brittle metal of crystalline structure, permanent at ordinary temperature, but at high heat it burns with a brilliant flame forming the trioxid, Sb_2O_3 . In cooling after liquefaction it expands, and this property makes it very valuable as an alloy. Its principal alloys are: type-metal (antimony, lead and tin) and britannia metal (antimony, copper and tin). Antimony is a poor conductor of heat and electricity. When acted upon by concentrated sulfuric or hydrochloric acid, it forms salts; by nitric acid, it is oxidized, forming oxids.

Compounds.—Antimony forms both “ic” and “ous” compounds, nearly all of which are decomposed by water. Tartar emetic (antimonii et potassii tartras) is the only official salt of antimony. It has the formula $2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ and is prepared by boiling antimonous oxid, Sb_2O_3 , with potassium bitartrate, filtering and evaporating the solution. Reaction: $\text{Sb}_2\text{O}_3 + 2\text{KHC}_4\text{H}_4\text{O}_6 = 2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$. Potassium antimonyl tartrate (its chemical name) is a white crystalline salt, soluble in hot water, slowly in cold water; used as an emetic and expectorant, it enters into the compound syrup of squills (syrupus scillæ compositus, 0.4%). Antimony forms salts much the same as described under arsenic: Stibin, SbH_3 ; several halogen salts, among which the trichlorid, SbCl_3 , commonly known as “butter of antimony,” finds much use in the arts and manufactures. It forms three oxids, Sb_2O_3 , Sb_2O_4 and Sb_2O_5 . It also forms two sulfids, Sb_2O_3 and Sb_2S_5 , and a number

of less important salts. In the U. S. P. (8th Rev.) antimony sulfid, purified antimony sulfid, antimony oxid, all of use in the preparation of other antimony compounds, but rarely used alone, have been dismissed. The tests described under arsenic, especially Marsh's and Fleitmann's test, of which the latter is valuable in that it differentiates the antimony from the arsenic, are valuable.

TIN.—Stannum, Sn, 117. Sp. gr., 7.3.

Occurrence.—Tin does not occur native, but almost entirely as oxid. Tin-stone, SbO_2 , commonly known as cassiterite, is its principal ore. When found in veins of rock, it is called mine-tin and when occurring in water beds, it is known as stream tin. It is sometimes found associated with other metals as a sulfid. Its principal mines are in Cornwall and England. In America it is found in California, South Dakota and New Hampshire.

Preparation.—The process of extracting tin from its ores ordinarily consists in three steps: (1) calcining; (2) washing; (3) reducing or smelting. The impure metal is cast into ingots which, when subjected to regulated heat, allow the tin to melt and run off, leaving behind the iron and copper.

Properties.—A soft, white metal, harder than lead, not acted upon by water or air at ordinary temperatures. Malleable, forming tin-foil, and, at temperatures just below melting, brittle. At high temperatures it burns, forming an oxid. It alloys with other metals, forming many useful ones, such as pewter, solder, brasses, bronzes, britannia and type-

metals, fusible alloys with bismuth, etc. It is used as a protective of iron and other metals, by covering them with a thin layer of tin. Tinware usually is made of sheet iron covered with tin. Its salts are used as mordants in dyeing and cloth printing. It forms two classes of compounds, the "ous" and the "ic," the first being divalent, the second tetravalent. It forms oxids—stannous oxid (SnO) and stannic oxid (SnO_2)—the former black and the latter white. These oxids form two acids with water—stannic acid (H_2SnO_2), and metastannic acid ($\text{H}_{10}\text{Sn}_5\text{O}_{15}$). The latter is also produced by acting with concentrated nitric acid on metallic tin. No salts of tin are official, and find no application in medicine. The salts are poisonous, but rarely used as poisons. Accidental cases of poisoning do occur in dye works, etc., in which cases emetics and demulcent drinks, like milk, should be administered freely.

Tests.—Tin may be detected by precipitating it from solution by hydrogen sulfid, converting it into oxid with nitric acid and weighing as such, if the quantity is desired.

CHAPTER XII.

HYDROGEN SULFID GROUP (Second Division).

BISMUTH, COPPER, CADMIUM AND MERCURY ("IC").

THIS is somewhat similar to the group just described. The metals to be discussed are precipitated by hydrogen sulfid, but members of this group are insoluble in ammonium sulfid solution, hence they are grouped together.

BISMUTH.—Bismuthum, Bi, 207. Sp. gr., 9.9. Bismuth differs from the other metals previously considered in that it occurs most commonly in the uncombined state. However, it is also found as an oxid (Bi_2O_3), as bismuth ochre, and as sulfid (Bi_2S_3) in bismuth glance. Its principal mines are in Saxony, where the metal is found associated with silver, cobalt and nickel.

Preparation.—The ores are heated in inclined iron pipes, and the melted bismuth run off from the other material. Subsequent purification is necessary.

Properties.—It is a white, lustrous metal with a reddish tint, very brittle, fusible at 268° Centigrade, volatile at higher temperatures, and at very high heat it burns, forming the trioxid Bi_2O_3 . It is unaffected by dry air at ordinary temperature, but is tarnished in moist air. It is attacked only slightly

by hydrochloric acid, but more readily by sulfuric and nitric acids. It is a poor conductor of electricity and it expands on cooling after fusion. If slowly cooled, obtuse rhombohedral crystals may be obtained.

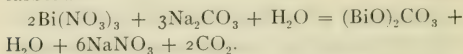
The metal is but little used except in alloys, to which it imparts ease of fusion and at the same time hardness. It plays the part of both a metal and a nonmetal under differing conditions. Its compounds are much used in medicine. It forms both "ous" and "ic" compounds, having the valence of 3 and 4, respectively. Most neutral salts of bismuth are converted into basic salts by water, and these latter are mostly used in medicine.

Bismuth Citrate (Bismuthi Citras U. S. P.)— $\text{BiC}_6\text{H}_5\text{O}_7$, should contain not less than 58% nor more than 60% of pure bismuth oxid. It is prepared by the action of the subnitrate on a solution of citric acid: $(\text{BiONO}_3 + \text{H}_2\text{O}) + (\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}) = \text{BiC}_6\text{H}_5\text{O}_7 + \text{HNO}_3 + 3\text{H}_2\text{O}$. It is a white, amorphous or crystalline powder, odorless, tasteless, insoluble in water, but soluble in ammonia water. It is used as the base of soluble bismuth and ammonium citrate—bismuthi et ammonii citras U. S. P. It is astringent and antiseptic.

Bismuth and Ammonium Citrate (Bismuthi et Ammonii Citras U. S. P.)—Similar in uses to the citrate. It is a scale salt prepared by dissolving the citrate in dilute ammonia water and subsequent scaling.

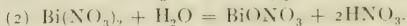
Bismuth Subcarbonate (Bismuthi Subcarbonas

U. S. P.)—Composition is variable. Purity, 90%. It is a white or pale yellow, odorless, tasteless and insoluble powder, decomposed by mineral acids. It is prepared from the subnitrate and an alkali carbonate:



Bismuth Subgalate (Bismuthi Subga'as U.S.P.)—Has a variable composition. It should contain from 52% to 57% bismuth oxid. It is an amorphous, bright-yellow, odorless, tasteless, insoluble powder, decomposed by strong acids. It may be prepared by mixing a warm solution of gallic acid with bismuth nitrate and glacial acetic acid; the substance is also designated "dermatol."

Bismuth Subnitrate (Bismuthi Subnitras U. S. P.)— BiONO_3 . Also called "magisterium" and basic bismuth nitrate. It should yield 80% of bismuth oxid, and is of varying composition. *Description:* It is a white, odorless, insoluble, almost tasteless powder, soluble in mineral acids, incompatible with alkaline carbonates, iodids, chlorids, tannates, etc. It is prepared by dissolving the metal in nitric acid and pouring the nitrate into a large quantity of water, whereby the subnitrate is precipitated. Thus:



Other reactions, depending on the quantity of water that enters the reaction, may be given.

Bismuth Subsaliolate (Bismuthi Subsaliolatas

U.S.P.)— $\text{Bi}(\text{C}_7\text{H}_3\text{O}_3)_3\text{Bi}_2\text{O}_3$. Basic bismuth salicylate should contain from 62% to 64% of bismuth oxid. It is a white, odorless, tasteless, permanent, insoluble powder, partly soluble in and decomposed by nitric and hydrochloric acids. It is prepared by precipitating bismuth nitrate with alkali, boiling, adding salicylic acid to the oxid so obtained, and heating to evaporation, washing and drying. Other valuable medicinal salts are the benzoate, oleate, tribromate, phenolate and many others of similar kind.

Bismuth forms four oxids—bismuth dioxid, Bi_2O_2 ; bismuth trioxid, Bi_2O_3 ; bismuth tetroxid, Bi_2O_4 ; and bismuth pentoxid, Bi_2O_5 . It also forms a hydroxid, but does not form a trihydrid. Most bismuth salts are tonic, astringent and antifermentative. They are largely employed in intestinal disorders. Poisonous symptoms observed after using bismuth salts are nearly always due to arsenical impurity.

Tests.—Neutral and acid solutions of the salt are precipitated by water. With sulfids it gives a black precipitate, alkali hydroxids give a white precipitate; iodids give a brown precipitate. Potassium sulphocyanate paper moistened with a bismuth solution turns yellow on drying.

COPPER.—Cuprum, Cu., 63.2. Sp. gr., 8.9

Occurrence.—It is found native in large quantities, notably in the Lake Superior region and in China, Japan and Sweden. In combination, it is exceedingly abundant and is found in many forms, chiefly as sulfid, chalcocite, pyrites, carbonate (malachite) and cuprite or oxid. Numerous methods of separating it

from its ores are employed, all depending upon the nature of the ore.

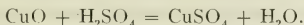
Properties.—It is a reddish-brown metal, lustrous, very tenacious and ductile, being readily drawn into fine wire. It is also very malleable, producing very thin leaves. It is fusible and volatile at very high temperatures producing an emerald-green vapor. It is readily attacked by nitric acid, slowly by hydrochloric and sulfuric acids in the air, also very slowly by air itself, forming a green, basic carbonate. Copper is second only to silver as a conductor of electricity, and is extensively used for all electrical purposes. It is also used in electrotyping and very largely in the form of alloys, the most important of which are those with zinc (brass and Muntz metal), with tin (gun metal, bronze and speculum metal), with aluminum (aluminum bronze) and with silver and gold, the respective coin metals.

Compounds.—Copper forms both “ous” and “ic” compounds. The cuprous oxid is the only important “ous” salt which occurs native, as red copper ore, Cu_2O . It is produced by the reduction of cupric chlorid (CuCl_2), and also in the alkaline copper solution (Fehling’s solution) with grape sugar. It is insoluble in water, easily affected by acids and fuses at red heat. Copper forms chlorid, hydroxid, oxid, nitrate, sulfate, carbonate and sulfid, the only one recognized officially being the sulfate.

Cupric Sulfate (cupri sulfas U. S. P.), $\text{Cu SO}_4, 5\text{H}_2\text{O}$.—Copper sulfate, blue vitriol, blue stone; purity, not less than 99.5%.

Description.—Transparent, large deep-blue crystals, efflorescent, odorless with metallic, astringent taste. Soluble in 2.2 parts of water, 3.5 parts of glycerin; insoluble in alcohol. Incompatible with fixed alkali hydroxids.

Preparation.—(1) By dissolving cupric oxid in dilute sulfuric acid, filtering, evaporating and crystallizing:



(2) By the action of hot, concentrated sulfuric acid on metallic copper:



(3) By roasting copper pyrite in the air, in which process the sulfate is formed in conjunction with the sulfate of iron. It is used as a caustic, astringent and emetic. A solution of cupric sulfate in which some ammonium chlorid has been dissolved, upon the addition of sodium hydroxid, forms cupric hydroxid. This dissolved in ammonia water forms Schweizer's reagent which dissolves cotton wool and other forms of cellulose, which can be reprecipitated from the solution by the addition of salts or acids.

The commercial compounds and pigments of copper are very important. Among these the following may be named: "*Paris Green*, chemically cupric acetoarsenite ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{CuO}_4\text{As}_2$); *Verdigris*, chemically copper subacetate, copper oxyacetate, basic acetate of copper ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{CuO} + 3\text{H}_2\text{O}$). Copper subacetate is prepared by exposing copper to the action of acetic acid and air, and recently the term verdigris was incorrectly applied to the

green carbonates which form on the surface of copper salts. *Scheele's Green* is the copper arsenite of commerce, a very valuable, though very poisonous pigment, employed in wall-paper printing, in book covers, etc. It is prepared by mixing solutions of copper sulfate and sodium arsenite, washing the bright-green precipitate obtained, and drying. *Brunswick Green* is a mixture of copper carbonate and chalk. *Brighton Green* is copper acetate mixed with chalk. *Mountain Green* is the native copper carbonate. *Neuwieder Green*, is a mixture of Schweinfurt green with gypsum and barium sulfates. *Green verdites* is the basic carbonate and oxid mixed with chalk.

Toxicology.—Copper salts are probably falsely credited with very poisonous properties, for such are likely due to arsenical contamination, or to the double salts of copper and arsenic. Albuminous drinks and emetics are indicated in cases of copper poisoning.

Tests.—Ammonia water produces a light-blue precipitate, changing to deep blue solution with excess. Hydrogen sulfid produces a black precipitate (CuS). Potassium cyanid produces a white precipitate. Minute quantities may be detected by taking up with dilute nitric acid, neutralizing with ammonia, again acidifying with acetic acid, and adding potassium ferricyanid. A red color indicates copper. Copper salts color Bunsen flame green, excepting the chlorid which colors it blue.

CADMIUM—Cd, 112. Sp. gr., 8.6. Cadmium never occurs uncombined and is found in but few ores, most often accompanying zinc, from which

it is obtained by distilling, it being more volatile than the latter.

Description.—It is a bluish-white metal similar to zinc, but more malleable and ductile. It melts at 320°C . Heated, it burns, forming brown oxid.

Compounds.—No compounds of cadmium are used in pharmacy. Its alloys are valuable commercially. The element is a dyad, forming hydroxid, oxid, chlorid, iodid, sulfate and sulfid. *Cadmium oxid* (CdO) is a brown salt; the sulfid (CdS) is a bright-yellow pigment valued as a paint. The iodid and bromid have been used in photography.

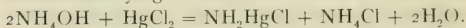
MERCURIC—MERCURY.—Mercury has been fully discussed in Chapter X (see page 79), and only the mercuric compounds that occur in this grouping need here be discussed. The mercuric compounds are more numerous and important. Mercury plays here the part of a dyad or divalent element, and mercuric compounds are always produced when the metal is dissolved in an excess of the acid. Mercuric chlorid is an important salt of mercury (*hydrargyri chloridum corrosivum*, U. S. P.), HgCl_2 , also called bichlorid, perchlorid, muriate and corrosive sublimate. .

Preparation.—By subliming a dry mixture of mercuric sulfate and sodium chlorid. $\text{HgSO}_4 + 2\text{NaCl} = \text{HgCl}_2 + \text{Na}_2\text{SO}_4$. The sublimed form is that of rectangular octahedra; while that crystallized from a solution assumes rhombic prism form. It is, therefore, dimorphous. It is soluble in 16 parts of water, 14 parts of glycerin, 3 of alcohol. In presence

of heavy metals it is reduced to the mercurous state (calomel). Its aqueous solution, treated with an alkaline hydroxid (lime water), produces a yellow precipitate of mercuric oxid (HgO), the liquid so produced being known as "yellow wash" (lotio flava, N. F., or "aqua phagedenica flava" of the ancients). *Yellow mercuric oxid* (hydrargyri oxidum flavum U. S. P.) is prepared by precipitating mercuric chlorid solution with sodium hydroxid. Reaction:



An orange-yellow, amorphous, insoluble powder, soluble in dilute acids. It is more active than the red oxid and therefore preferred in skin preparations and eye salves. *Ammoniated mercury* (hydrargyrum ammoniatum U. S. P.), NH_2HgCl , white precipitate, ammoniated chlorid of mercury, amidochlorid of mercury, is produced by mixing solutions of mercuric chlorid and ammonia water, washing the precipitate with water containing a little ammonia and drying. Reaction:



It is an insoluble, white powder, soluble in warm hydrochloric or nitric acids.

Red mercuric iodid (hydrargyri iodidum rubrum U. S. P.), HgI_2 , red iodid, biniodid, deutoiodid, mercuric iodid.

Preparation.—Made by mixing solutions of mercuric chlorid and potassium iodid, washing free from chlorids and drying the precipitate. Reaction:



It is a scarlet-red powder, usually amorphous,

sometimes found in octahedral and rhombic needles, hence is dimorphous. It dissolves in a solution of potassium iodid or mercuric chlorid. It is nearly insoluble in all other solvents. It is an ingredient of Donovan's solution (liquor arseni et hydrargyri iodidi U. S. P.).

Red mercuric oxid (hydrargyri oxidum rubrum U. S. P.), HgO , red precipitate, peroxid.

Preparation.—By heating nitrate of mercury crystals till nitrous fumes cease to evolve. It is a red powder or crystalline scale. By dissolving it in hydrochloric acid and evaporating, the mercuric chlorid is obtained. The difference in the two oxids—yellow and red—lies in the methods of their preparation, the former made by precipitation, the latter by ignition of the nitrate. Students should remember that there is one each official—a mercurous and a mercuric chlorid and iodid—but that both the oxids have the same composition, both being mercuric salts. They are both insoluble in ordinary solvents, but soluble in dilute acids. Among the unofficial mercuric compounds are the cyanid (HgCN_2) a very poisonous, opaque-white mass, soluble in 12 parts of water; turpeth mineral (hydrargyri subsulfas flavus), $\text{Hg}(\text{HgO})\text{SO}_4$, basic sulfate of mercury, a lemon-yellow powder used as an emetic; mercuric nitrate $\text{Hg}(\text{NO}_3)_2$, prepared by careful solution of mercury or of the oxid in nitric acid. It is used as a reagent in "Liebig's urea test" and for preparing other compounds of mercury.

CHAPTER XIII.

IRON, ALUMINUM, CHROMIUM.

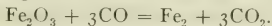
The *ammonium sulfid group* embraces those metals which are precipitated by ammonium sulfid solution. The entire group is subdivided into two divisions: iron, aluminum and chromium comprise the first division, and cobalt, nickel, manganese and zinc make up the second division. The reason for this division is that while ammonium sulfid precipitates all the seven metals, it does not form the same compounds with all. Thus, the metals of the first division are precipitated as hydroxids, while those of the second division are precipitated as sulfids. Moreover, the first division may be precipitated by ammonium hydroxid in the presence of ammonium chlorid, which latter prevents the precipitation of the remaining metals. Thus, the first three metals are separated from the second division as hydroxids. If ammonium sulfid is now added to the entire division, it changes the iron hydroxid to a sulfid, but does not affect the remaining two.

IRON.—Ferrum, Fe, 56. Sp. gr., 7.1 to 8.1.

Occurrence.—Iron is found native in small quantities in the meteorites, in some to the extent of 98%. It is a metal of great importance and is widely distributed. The ores that contain iron in combination are numerous, but only few of the more important

ones will be here mentioned. *Magnetite*, Fe_3O_4 , consists of ferroso-ferric oxid = FeO , Fe_2O_3 ; *Hematite*, chiefly ferric oxid, Fe_2O_3 ; *Limonite* (or brown hematite), a variable mixture of the oxid and hydroxid, and *Siderite* (spathic iron), consists of ferrous carbonate, FeCO_3 . The sulfur ores, as, for example, the iron pyrites (FeS_2), are not well adapted to extraction, but are valuable for the manufacture of the acids of sulfur.

Preparation.—Iron exists in three forms—as cast iron, wrought or malleable iron and steel. To understand the relationship existing between these it is best to study the processes of their manufacture. The ore in case of the hematites is first calcined to remove the water, and in case of the carbonate ores, the carbon dioxid. The calcined ore consists chiefly of ferric oxid and it is smelted in blast furnaces with limestone and coke. Limestone forms a fusible slag with the silica present while the coke burns in the hot air introduced by the blast tubes, forming carbon monoxid, which serves as a reducing agent of the glowing ferric oxid to metallic iron. Reaction:



The smelting is continued uninterruptedly, the furnace being supplied with fresh material so that molten iron is continuously formed at the bottom of the furnace from which it is drawn off from time to time at a special tap-hole which is temporarily blocked up with clay, while the slag of calcium silicate floating on the surface of the molten iron is allowed to flow away as soon as it forms. The iron is run into

channels made in sand, in which it solidifies in bars known in commerce as *pig iron* or *cast iron*. Since cast iron is produced in contact with carbon, it contains a small amount of this element, both as ferric carbide and in the free state. Besides these, it usually contains silicon, phosphorus, some sulfur and a little manganese. Cast iron, containing from 2 to 5% of carbon, is comparatively brittle, easily fusible and cannot be welded. By removing the silicon, phosphorus, sulfur, etc., which exist there as impurities, we produce *wrought iron* which is a comparatively pure form of iron. This is done by piling pig iron on the bed of a reverberatory furnace previously lined with ferric oxide, melting and thoroughly stirring the iron, when the impurities will become oxidized through the ferric oxide lining in the furnace, and will escape as sulfur dioxide, carbonic acid, phosphorus oxide, etc. Wrought iron contains less than 0.2% of carbon, is extremely malleable, infusible in the ordinary furnace, tough, and when heated to white heat it becomes pasty, so that two pieces when brought together while hot and hammered can be *welded* into one. *Steel* is produced by heating bars of wrought iron imbedded in layers of charcoal for several days, in which process, although the iron never melts, the carbon permeates it to the extent of 0.5 to 1.4%. This process is now employed only for the production of high-quality steel, and has been superseded by the cheaper *Bessemer* process. This consists in blowing a current of air through molten cast iron until the impurities are burned out. To this

purified metal a certain proportion of pure pig iron, preferably that containing manganese, like *spiegeleisen* or *ferromanganese*, is added, together with a certain quantity of carbon. The carbon converts the iron into steel and the manganese serves to neutralize the untoward effects due to the small quantities of the oxids present. Steel is now manufactured largely by the so-called "open hearth" method or Siemens-Martin process. This process consists in fusing cast iron in a reverberatory furnace much as in the puddling process, next adding wrought iron to it and a small quantity of spiegeleisen, until the percentage of carbon is raised from 0.3 to 1.4%.

Steel contains from 0.3 to 1.5% of carbon which is chemically combined with the iron. It has a fine-grained structure; it is malleable and fusible in a furnace with a good draught; it melts at about 1400° C. Its most important property is that it can be tempered, that is, its hardness may be altered by the rate at which it is cooled. If, for example, when heated to redness, it is plunged into cold water, it is very brittle, but hard enough to scratch glass; if, however, it be allowed to cool gradually, it is almost as soft and malleable as wrought iron. From the above it will be seen that the tensile strength of pure iron is greatly increased by the admixture of small quantities of carbon, and the so carbonized iron is called steel.

Spiegeleisen (mirror iron) is a white, very crystalline cast iron, containing manganese as its chief constituent.

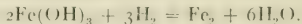
Description.—Iron is a soft, white, lustrous metal with greatest magnetic and tenacious power. It fuses with difficulty, but welds easily. It is fibrous in structure, but becomes crystalline in time from continuous vibrating or jarring, in which case it has much less tenacity. In dry air it is oxidized only at high temperature. It will not oxidize in pure water, but in moist air or when placed in water which has absorbed CO_2 from the air, it oxidizes quickly, the change being commonly called “*rusting*.” In contact with magnets, it becomes itself magnetic, but only tempered steel will retain this property for any length of time. Hydrochloric and sulfuric acids dissolve it freely and dilute nitric acid fairly easily, but concentrated nitric acid stops all solution till the “passive” condition is removed by heat or by contact with certain metals.

Compounds.—Iron forms both “ic” compounds, in which it is trivalent, and “ous” compounds, in which it is divalent.

It is official in two forms:

Iron (ferrum U. S. P.), metallic iron in the form of fine, bright and non-elastic wire (card teeth); and

Reduced iron (ferrum reductum U. S. P.), iron by hydrogen, alcoholized iron, Quevennes iron, containing at least 90% pure iron. It is a fine, grayish-black powder, made by heating iron hydroxid in hydrogen. Reaction:



Saccharated iron carbonate (ferri carbonas saccharatus U. S. P.) should contain not less than 15%

of FeCO_3 . It is a greenish-gray powder, sweetish, iron-like taste, not permanent, and should be kept in small, closely stoppered bottles. It is a mixture of sugar and ferrous carbonate, the latter prepared by double decomposition between ferrous sulfate and sodium bicarbonate. Reaction:



The carbonate of iron is an ingredient in the pill, mass and iron mixture of the U. S. P. preparations.

Iron sulfate (ferri sulfas U. S. P.), $\text{FeSO}_4 + 7\text{H}_2\text{O}$. Green vitriol, copperas, ferrous sulfate. Large, bluish-green colored crystals, soluble in 0.9 parts of water, and containing at least 99.5% of FeSO_4 . It is made by dissolving iron in dilute sulfuric acid: $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2$. It is used as a disinfectant in the arts and for the production of the official dried and granulated iron sulfates.

Dried ferrous sulfate (ferri sulfas exsiccatus U. S. P.), FeSO_4 . A white or gray powder, made by heating ordinary ferrous sulfate until it loses 35% in weight. It should be kept well stoppered.

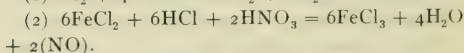
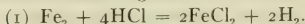
Granulated ferrous sulfate (ferri sulfas granulatus U. S. P.), $\text{FeSO}_4, 7\text{H}_2\text{O}$, was official in the U. S. P., '90, as "precipitated" ferrous sulfate. It is merely a granular form of ferrous sulfate made by dissolving the commercial salt in hot water containing a little sulfuric acid, filtering, evaporating, chilling suddenly, draining the salt on a filter, washing with alcohol and permitting it to dry in an atmosphere of alcohol.

Other ferrous compounds are the lactate ($\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2$), tartrate ($\text{FeC}_4\text{H}_4\text{O}_6$), phosphate (Fe_3 -

(PO_4)₂), oxalate (FeC_2O_4), chlorid (FeCl_2), iodid (FeI_2), this last salt being the ingredient of the official syrup and pil of iron iodid (syrupus ferri iodidi); oxid (FeO) and hydroxid ($\text{Fe}(\text{OH})_2$), all possessing the usual properties of iron combined with the characteristics of the acid from which formed.

The ferric compounds are more numerous and important than the ferrous compounds.

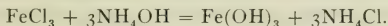
Ferric chlorid (ferri chloridum U. S. P.), $\text{FeCl}_3 + 12\text{H}_2\text{O}$, muriate, perchlorid, or sesquichlorid of iron. Orange-yellow, crystalline masses or crusts, made by crystallizing a properly oxidized solution of ferric chlorid. A very deliquescent salt used as a chalybeate. It is made by dissolving iron wire in HCl and oxidizing the solution with HNO_3 :



An aqueous solution of ferric chlorid is official (liquor ferri chloridi U. S. P.). This solution should contain about 37.8% of anhydrous FeCl_3 , corresponding to about 62.9% of the crystallized salt. A tincture of ferric chlorid (tinctura ferri chloridi U. S. P.), made by diluting the solution with alcohol, is also official. The tincture should contain at least 13.28% of anhydrous salt which corresponds to 4.6% of metallic iron.

Ferric hydroxid (ferri hydroxidum U. S. P.), $\text{Fe}(\text{OH})_3$, ferric hydrate, peroxid, hydrated ferric oxid. Prepared by precipitating a solution of ferric chlorid with ammonia water and washing free from

the ammonium chlorid formed; a brownish magma results. Reaction:



Ferric hydroxid with magnesium oxid (ferri hydroxidum cum magnesi oxido U. S. P.)—"arsenic antidote." This should be freshly made if it is to be used as an antidote in arsenical poisoning.

Preparation.—By rubbing MgO , 10 gm., in H_2O , 800 c.c., gradually adding a mixture of ferric tersulfate solution, 40 c.c., and H_2O , 125 c.c., and mixing thoroughly. Dose, 120 c.c.

Ferric hypophosphite (ferri hypophosphis U. S. P.), $\text{Fe}(\text{PH}_2\text{O}_2)_2$. A grayish-white powder, nearly tasteless and slightly soluble. Used in making syrup of hypophosphites comp. (syrupus hypophosphitum compositus U. S. P.). Used as a hematinic.

Iron and ammonium sulfate (ferri et ammonii sulphas U. S. P.), $\text{FeNH}_4(\text{SO}_4)_2 + 12\text{H}_2\text{O}$. Iron and ammonia alum, iron alum. Pale violet, octahedral crystals, odorless, styptic taste, efflorescent. Should contain 99.5% pure salt, corresponding to 11.5% of iron. Prepared by dissolving ammonium sulfate in solution of ferric tersulfate, evaporating and crystallizing. Reaction:



SCALE SALTS.—These compounds are usually prepared by dissolving ferric hydroxid in a corresponding organic acid, evaporating to syrupy consistence and spreading on glass plates, from which it flakes or scales on cooling. All scale salts are ferric salts.

There are nine official scale salts: Soluble ferric phosphate (ferri phosphas solubilis), iron 12%; soluble ferric pyrophosphate (ferri pyrophosphas solubilis), iron 10%; ferric citrate (ferri citras), corresponding to 16% iron; iron and ammonium citrate (ferri et ammonii citras), corresponding to 16% iron; iron and ammonium tartrate (ferri et ammonii tartras), corresponding to 13% iron; iron and potassium tartrate (ferri et potassii tartras), 15% iron; iron and quinine citrate (ferri et quininæ citras), 13.5% iron; soluble iron and quinine citrate (ferri et quininæ citras solubilis), 13.5% iron; iron and strychnine citrate (ferri et strychninæ citras), 16% iron. The soluble phosphate and pyrophosphate are green in color, the other seven being garnet-red to reddish-brown. With the exception of iron citrate and the iron and quinine citrate, which are very slowly soluble in water, all the scale salts of iron contain alkalin citrate or tartrate, purposely added to enhance their solubility, and are usually designated as "soluble."

All the official liquors of iron contain ferric salts.

Dialysed iron (ferrum dialysatum) is made by dissolving crystalline ferric chlorid in the solution of ferric chlorid and subjecting the mixture to dialysis. By this process the remaining free acid is removed, leaving a colloidal basic salt composed of 99% of ferric hydroxid and 1% of hydrochloric acid.

Iron and its salts are not poisonous.

Tests.—Iron may be detected by a red precipitate with ammonium hydroxid, a brownish-black precipitate with hydrogen sulfid, etc.

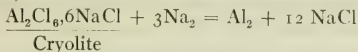
Distinctive tests between ferric salts and ferrous salts:

REAGENT	FERRIC SALTS.	FERROUS SALTS.
Potassium ferrocyanid,	Dark-blue precipitate	Light-blue precipitate
Potassium ferricyanid,	Brownish color; no precipitate formed.	Dark-blue precipitate.
Potassium sulfocyanid,	Dark, blood-red color- ation.	No change of color (with impure ferrous salts turns reddish).
Alkalis,	Brownish precipitate.	Green precipitate, turning brown on the surface.

ALUMINUM, Al, 27. Sp. gr., 2.5.

Occurrence.—Aluminum is the most abundant metal, and of all the elements it is only exceeded in abundance by oxygen and silicon. It is never found native and until comparatively recently it was difficult to extract from its combinations. It occurs as a silicate in clays, kaolin, feldspars, micas, granite, porphyry and many crystalline rocks. As an oxid (Al_2O_3), it is found in the ruby, sapphire and in corundum and emery. Cryolite is the double fluorid of aluminum and sodium ($\text{Al}_2\text{Cl}_6, 6\text{NaCl}$), and bauxite is an hydrated oxid ($\text{Al}_2\text{O}_3, \text{H}_2\text{O}$), both of which are largely used for the production of aluminum.

Preparation.—(1) By reducing of the ores with carbon by the intense electric-furnace heat; (2) by treating cryolite with metallic sodium (Deville's process). Reaction:



Properties.—A white, silvery metal, very tenacious, malleable and ductile. It is very light, but strong and rigid; is an excellent conductor of heat and electricity, almost equal to silver in this respect. It is affected but little by air, gases or ordinary

acids, but is readily dissolved by caustic alkalis. It melts at 625° C. It does not tarnish in the air and is not affected by hydrogen sulfid. Aluminum forms valuable alloys and is much used in the arts. It is also becoming of great value in numerous commercial and domestic wares.

Aluminum bronze (copper, 90; aluminum, 10), is one of the alloys of aluminum valued for castings and superior to brass in tensile strength. Steel is improved by the addition of 0.1% of aluminum.

Aluminum acts as a trivalent element.

The alums are important compounds of aluminum. The general formula of the alums is $RR'(SO_4)_2 \cdot 12H_2O$ —the R representing Al, Cr, Fe or Mn, and R' one of the alkali metals. They all crystallize as octahedra.

Alum (alumen U. S. P.), $AlK(SO_4)_2 + 12H_2O$. Alum, potash alum. Purity, 99.5%. Large, odorless, colorless, octahedral crystals, with astringent taste. Soluble in 9 parts of water. Incompatible with alkali hydroxids, carbonates and phosphates, and chlorids of the heavy metals. Other alums are the *ammonia alum*, $AlNH_4(SO_4)_2 + 12H_2O$, similar to potash alum, a double sulfate of ammonium; *iron alum*, *chrome alum*, *manganese alum*, etc., in which these respective metals replace the aluminum in the molecule.

Preparation.—Official alum is made by calcining alum-shale (alum clay, aluminum silicate) with iron pyrites, which operation results in the formation of sulfuric acid, which acting on the silicate

produces aluminum sulfate. This, together with the sulfates of iron is extracted with water. In this liquid potassium chlorid is dissolved which interacts with the iron sulfates, becoming converted into potassium sulfate, which combines with aluminum sulfate and which crystallizes with 12 molecules of water of crystallization.

Exsiccated Alum (alumen exsiccatum U. S. P.), $\text{AlK}(\text{SO}_4)_2$, dried or burnt alum, alumen ustum. Purity, 99%. A dry, porous mass or powder, odorless, sweetish, astringent taste, nearly twice as strong as the official alum, attracting moisture. It is soluble in 17 parts of water, 1.5 parts of boiling water.

Preparation.—By merely driving off the water of crystallization from alum. The alums are all used as caustic astringents.

Aluminum salts precipitate organic colors, forming with them pigment "lakes," etc. This important property is utilized in dyeing, where alumina ($\text{Al}(\text{OH})_3$) becomes deposited in the material to be dyed and acts as a "mordant," "binder" or "fixer" of the dyes employed.

Aluminum hydroxid (alumini hydroxidum U. S. P.), $\text{Al}(\text{OH})_3$, alumina. A white, light, amorphous powder, permanent, odorless and tasteless, made by treating a soluble salt of aluminum with an alkali hydrate or carbonate: $2\text{AlK}(\text{SO}_4)_2 + 3\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + \text{K}_2\text{SO}_4 + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2$. It is used as a mechanical protective filtering medium and for preparing the sulfate of aluminum.

Aluminum sulfate (alumini sulphas U. S. P.), Al_2 -

$(\text{SO}_4)_3 + 16\text{H}_2\text{O}$; 99.5% pure. It is a white, crystalline powder, flakes or fragments, odorless, sweetish, astringent taste, soluble in one part water. Loses crystalline form at 200°C . In medicine, aluminum sulfate should not be confounded with alum. A commercial aluminum sulfate (alum cake) is sometimes called "concentrated alum" and contains but 12 molecules of water of crystallization.

Aluminum forms chlorid (AlCl_3), oxid (Al_2O_3), bromid (AlBr_3), iodid (AlI_3), fluorid (AlF_3). *Spinel* is native magnesium aluminate (MgAl_2O_4). Other aluminates are known, but they find but little application in the arts.

The most important utilization of the aluminum clays is in *pottery* and *ceramics*. Thus, porcelain, earthenware and stoneware are prepared from native aluminum compounds; *porcelain* from kaolin, feldspar or quartz; *earthenware* from clay or feldspar and silica; *stoneware* from clay containing ferric oxid and lime. Cements and mortars, which are manufactured from the *lime-clays* and similar artificial mixtures, may here be mentioned:

When burnt (calcined) lime is treated with water, it "slakes." When such slaked lime is alone used as a mortar, it *sets* and slowly hardens, but in the process of setting it cracks, thus making its use as mortar unprofitable. When, however, it is mixed with some substance which tends to counteract this excessive shrinkage, it forms a good mortar. Sand or silica (SiO_2) is a good admixture for this purpose if mixed with the lime in proper proportions. The

setting of mortar is due to the loss of moisture (water is formed in the process of setting, thus: $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$, this accounting for the persistent dampness of newly built houses in which the mortar is setting), and the hardening is due to absorption of carbon dioxid from the air which in time converts the lime to limestone. In this reaction the lime superficially attacks the surfaces of the sand grains, converting these into calcium silicate which further solidifies the mortar, making it in time a stone-like mass. For this purpose angular sand grains are preferred to the well-rounded pebbles.

Roman cement is made by calcining calcareous clay which must be "fat" (free from magnesia) at a temperature just below sintering.

Portland or hydraulic cement is made by calcining mixtures of limestone with clay (or other materials containing aluminum, silica and lime) and finely grinding the resulting clinker-like mass. When mixed with water, cement *should not* be allowed to *stand*, but should be applied at once. The setting of cement is supposed to be due to the formation of crystalline silicates and aluminates of calcium, which form a hard stone-like mass. Good Portland cement should contain from 55 to 60% of lime, 22 to 26% of silica and 7 to 8% of alumina.

Concrete consists of hydraulic cement mixed with crushed rock or pebbles.

Aluminum and its salts are nonpoisonous.

Tests.—Aluminum may be detected by precipitation with ammonia, as hydroxid soluble in alkali

hydroxids and reprecipitated by NH_4Cl ; also by fusion on charcoal with cobalt nitrate, giving a rich blue color to the mass.

CHROMIUM, Cr, 52. Sp. gr., 6.8.

Occurrence.—Chromium is not found free, but occurs most commonly in chromite, also called “chrome iron ore,” a ferroschromic oxid, $\text{Cr}_2\text{O}_3\text{-FeO}$. It is separated with difficulty from the ore, and is usually prepared by the reduction of chromium sesquioxid with charcoal in the electric furnace.

Properties.—It is a hard, glistening, steel-gray metal, very fusible, magnetic at low temperatures, oxidizes only at a high heat, is soluble in hydrochloric acid and strong alkalis.

Alloys of chromium are admixed with steel to increase the strength of the latter.

Chromium acts both as an acid and a basic radical, forming compounds in each capacity. As a base it exerts trivalent, tetravalent and hexavalent properties, forming “ous” and “ic” salts. It forms two oxids well defined—the chromic oxid (Cr_2O_3), a green, insoluble powder used as pigment in glass and porcelain making; and *chromic anhydrid* or trioxid (chromii trioxidum) (CrO_3), previously improperly known as “chromic acid.”

Preparation.—From potassium dichromate and sulfuric acid: $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 = 2\text{CrO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$. Saffron-colored needle crystals, very hygroscopic, very strong oxidizing agent. Decomposes organic solvents, such as alcohol or glycerin, with dangerous violence. It is used as a caustic.

With water it forms chromic acid (H_2CrO_4), from which a series of salts are produced: $\text{H}_2\text{O} + \text{CrO}_3 = \text{H}_2\text{CrO}_4$. A second acid may be produced by removing water from ordinary chromic acid. Thus:



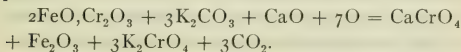
the series of salts are known as dichromates (bichromates), and the principal one is the potassium salt—*potassium dichromate*, also called bichromate or red chromate (potassii dichromas U. S. P.), $\text{K}_2\text{Cr}_2\text{O}_7$ ($\text{K}_2\text{CrO}_4, \text{CrO}_3$).

Potassium dichromate is prepared from potassium chromate and sulfuric acid. Reaction:



It occurs as a reddish, crystalline salt.

Potassium chromate, K_2CrO_4 yellow chromate of potash, is made by roasting chrome iron ore with potassium carbonate and lime. Reaction:



The yellow chromate is more soluble than the dichromate; both salts are much used in the arts and chemically as strong oxidizing agents, especially the latter. *Lead chromate* (chrome yellow), PbCrO_4 , is found native as *crocoisite*. It is prepared by precipitating soluble lead salt with potassium dichromate; *barium chromate*, BaCrO_4 , is prepared similarly. Both are used as yellow pigments.

Chromic sulfate (chrome alum) has the formula $\text{CrK}(\text{SO}_4)_2, 12\text{H}_2\text{O}$. By adding ammonia to chrome alum the greenish hydroxid $\text{Cr}(\text{OH})_3$ is obtained, which on ignition yields the sesquioxid Cr_2O_3 , which,

under the name of *chrome green*, is employed as a green pigment. Another pigment is "Guignet's Green," a hydroxid obtained by heating potassium dichromate with boric acid and extracting with water. Both the yellow and green pigments of chromium, being very insoluble, are highly valued and some of these are used in the printing of the United States paper money.

Chromyl chlorid, CrO_2Cl_2 , a red, fuming liquid, is obtained by distilling a mixture of potassium dichromate and sodium chlorid with sulfuric acid.

Chromic chlorid, Cr_2Cl_6 , is obtained by acting with chlorin on a heated mixture of chromic oxid and carbon.

Toxicology.—Chromium compounds, especially the dichromate of potassium, are irritant poisons and may produce either acute or chronic poisoning. Emetics should be promptly administered followed by magnesium carbonate and demulcent drinks.

Tests.—Soluble chromium compounds may be detected by the greenish precipitate formed with ammonia, or by the solutions of soluble lead salts which produce the yellow chromate of lead. The insoluble salts may be recognized by the borax bead which, in the oxidizing flame, is reddish when hot, yellowish-green when cold, and in the reducing flame it is green.

CHAPTER XIV.

COBALT, NICKEL, MANGANESE, ZINC.

As already stated, these metals comprise the second division of the ammonium sulfid group. They are precipitated by ammonium sulfid, in the presence of ammonia water and ammonium chlorid, as sulfids and separated as such. The ammonium chlorid plays the part of a solvent for the metals of the later groups and prevents their precipitation.

The first two metals, cobalt and nickel, are of but little value pharmaceutically and have no official preparations. In chemistry, the arts and manufactures, however, they are more important. Manganese and zinc, on the other hand, are of much more importance, both pharmaceutically and in the arts.

COBALT, Co., 59.5. Sp. gr., 8.9.

Occurs native only in meteorites. Its most important ores are *spieess-cobalt*, or "smaltine," CoAs_2 ; cobalt *glance*, or "cobaltite," $\text{CoAs}_2\text{CoS}_2$, and the arsenical sulfid, CoAsS .

The metal is obtained by reduction of the chlorid with hydrogen, but the processes employed are complicated.

Cobalt is a lustrous-white, tenacious metal, malleable and, when heated, quite ductile. It melts with difficulty. It becomes magnetic and holds this

property even when heated to redness. It is unaltered in the air except in very fine powdered form. It forms three oxids: cobaltous oxid, CoO , a drab-colored powder, obtained by reducing the sesquioxid; cobaltic oxid, Co_2O_3 , and cobalto-cobaltic oxid, Co_3O_4 , also several others of less importance. It also forms cobaltic hydroxid, $\text{Co}(\text{OH})_2$, when precipitated with the caustic alkalis, cobaltous chlorid, CoCl_2 ; cobaltous sulfate, $\text{CoSO}_4 + 7\text{H}_2\text{O}$, etc.

Cobalt also forms a large number of complex ammoniacal cobalt compounds, which will be mentioned later.

When cobalt compounds are fused with borax, a clear, blue, glassy bead is produced, and a similar blue is imparted in the same way to ordinary blue glass, due to the formation of silicates of cobalt. This cobalt silicate, finely ground, forms a pigment known as "smalt," and is employed in decorative arts.

Cobalt chlorid in solution forms "sympathetic inks"—invisible until heated. With NaOH , the salts of cobalt yield a blue precipitate, which on boiling is converted into the hydroxid.

NICKEL, Ni , 58.7. Sp. gr., 8.9.

The properties of nickel are so similar to cobalt as to require no special discussion. The principal ores of nickel are *niccolite*, Ni_2As_2 , and nickel glance, $\text{NiAs}_2\text{NiS}_2$. The metal is obtained by reducing the oxid with carbon or by hydrolysis. The compounds of nickel correspond to those of cobalt. Nickelous oxid, NiO ; chlorid, NiCl_2 ; sulfid, NiS . Nickel finds much use in alloys and electroplating.

Nickel imparts a red-brown color to the borax bead in the oxidizing flame, and gray opaque in the reducing flame. The presence of cobalt masks these colors entirely and must be removed before a flame-test for nickel is made.

MANGANESE, Mn, 55. Sp. gr., 7.2

Never found native in the metallic state, but it is widely distributed in combination with oxygen as *pyrolusite*, MnO_2 ; *braunite*, Mn_2O_3 ; *hausmannite*, Mn_3O_4 ; also as *manganite*, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and as *spar*, MnCO_3 . The metal may be obtained by reducing its ores with charcoal.

Manganese is a hard, steel-gray, brittle metal, oxidizes readily in the air, and is readily acted upon by hydrochloric and sulfuric acids. The metal finds but little use in the free state, but as an alloy with iron, *spiegeleisen* and *ferromanganese*, it is used in steel making.

Manganese combines the properties of both a metal and an acid. Manganese forms "ous" compounds, MnR_2 ; "ic" Mn_2R_6 , and salts of *manganic acid*, H_2MnO_4 , called *manganates*. It forms the usual series of salts of all three types.

The precipitated black oxid (mangani dioxidum precipitatum U. S. P.), MnO_2 , should be at least 80% pure.

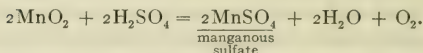
Description.—Heavy black powder, odorless, permanent. Used as a *catalytic* to produce oxygen from potassium chlorate, and, heated with sulfuric acid, loses its own oxygen and forms manganous sulfate, commonly known as *pink vitriol*.

Manganese hypophosphite (mangani hypophosphis U. S. P.), $\text{Mn}(\text{PH}_2\text{O}_2) + \text{H}_2\text{O}$, is official.

Description.—Pinkish-white crystalline powder, odorless and tasteless, soluble in 6.5 parts water; at least 79% pure. The hypophosphite is used as a tonic and enters into the syrup hypophosphites compound.

Manganese sulfate (mangani sulphas U. S. P.), $\text{MnSO}_4 + 4\text{H}_2\text{O}$. Manganese sulfate. Pink vitriol. Purity, 99.5%.

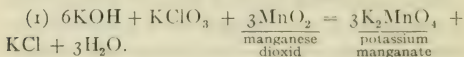
Preparation.—From the dioxid with sulfuric acid;
Reaction:



Description.—Transparent, pale, rose-colored crystals, odorless, but bitter astringent in taste, readily soluble, used as a hematinic.

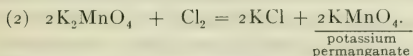
The *derivatives of manganic acid*, are analogous to salts of sulfuric acid, the manganese acting as a hexad. The manganates are not permanent, but are readily convertible into the *permanganates*. The most common permanganate is the salt of potassium.

Potassium permanganate (potassii permanganas U. S. P.), KMnO_4 , is prepared from the dioxid. The reaction takes place in two stages:



The green manganate of potash, K_2MnO_4 , is then changed to permanganate by extracting the mass

with boiling water, cooling and passing chlorin into it:



The solution is then crystallized. The permanganate forms dark-red, almost black, rhombic prisms. It has very strong oxidizing properties, and finds much use in this capacity as a disinfectant, deodorant and antiseptic solution. It decomposes with organic substances; pills of the permanganate are best made by triturating the salt with kaolin and massing with petrolatum.

ZINC, Zincum, Zn, 65. Sp. gr., 6.8–7.2.

This element always occurs in combination. Its compounds are only fairly abundant. The most important zinc ores are the carbonate, *calamine*, ZnCO_3 ; the sulfid, or *zinc blende*, *sphalerite*, ZnS , and *red-zinc ore*, ZnO , found in New Jersey, as is also *franklinite*, $(\text{ZnFe})\text{OFe}_2\text{O}_3$.

The process of extraction usually consists of two steps: (1) roasting to convert into an oxid, and (2) mixing this with carbon and igniting in earthenware retorts, and thus reducing the oxid. The processes vary according to the nature of the ores. The crude metal so obtained is known as “spelter,” and is contaminated with iron, lead, arsenic, cadmium, etc. It is purified from these by a second distillation. Arsenic is a commonly found impurity, even in the better grades.

Zinc is a bluish-white, highly crystalline and brittle metal which can be pulverized. (*Zinc-dust* is so

prepared.) When heated between 150° and 200° C., zinc is malleable and ductile, and at still higher temperatures it again becomes brittle. Zinc fuses at 412° C., and distills at 940° C. It dissolves readily in dilute acids forming corresponding salts and liberating the hydrogen of the acids. It is also soluble in alkaline hydroxids, forming *Zincates*.

Since it is not affected by the air, it finds much use as an outside coating, such as the "galvanizing" of iron, etc.

Zinc is official (*Zincum*) and is required to be at least 99% pure and free from arsenic.

Granulated zinc is made by pouring molten zinc into water.

The zinc alloys with copper, such as *brass*, are valued and are much used. It also alloys with tin, copper and antimony in all proportions, but with lead and bismuth in definite proportions only.

German silver is an alloy of copper, zinc and nickel.

The present Pharmacopœia recognizes the following zinc compounds:

Zinc acetate (*Zinci acetat* U. S. P.), $\text{Zn}, (\text{C}_2\text{H}_3\text{O}_2)_2 - 2\text{H}_2\text{O}$; 99.5% pure.

Zinc bromid (*zinci bromidum*), ZnBr_2 ; 97% pure.

Zinc carbonate (*zinci carbonas precipitatus*), which should yield not less than 72% of zinc oxid.

Zinc chlorid (*zinci chloridum*), ZnCl_2 ; 99.5% pure.

Zinc iodid (*zinci iodidum*), ZnI_2 , when anhydrous, should contain not less than 98% of pure zinc iodid.

Zinc oxid (*zinci oxidum*), ZnO ; at least 99.5% pure.

Zinc phenolsulfonate (zinci phenolsulphonas), $\text{Zn}(\text{C}_6\text{H}_5\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$; the uneffloresced crystals should contain at least 99.5% of the pure salt.

Zinc stearate (zinci stearas), $\text{Zn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$.

Zinc sulfate (zinci sulphas), $\text{ZnSO}_4 + 7\text{H}_2\text{O}$; 99.5% pure, "white vitriol."

Zinc valerate (zinci valeras), $\text{Zn}(\text{C}_5\text{H}_9\text{O}_2)_2 + 2\text{H}_2\text{O}$; 99% pure.

Of the above zinc salts, all are *soluble in water* and *poisonous*, except the carbonate, stearate and oxid. The last of these three finds much use in paints as a pigment, together with lead carbonate, to give the latter greater lasting qualities.

The zinc salts are *prepared* by acting upon the metal or its oxid or carbonate with the corresponding acid. The action of the zinc salts is due largely to the acid present in the compound and they are therefore astringent, antiseptic or disinfectant, as the case may be.

Toxicology.—All soluble zinc salts, as stated, are poisonous. The chlorid is used by tinsmiths, also in embalming and as "Burnett's disinfecting fluid." In all these it acts as corrosive. The best zinc antidotes are soap, milk and soluble alkali carbonates, or substances containing tannin, such as tea or coffee.

Tests.—With alkaline carbonates or hydroxids, zinc compounds in solution give a white precipitate soluble in excess of the reagent. Potassium ferrocyanid gives a yellowish-white precipitate, insoluble in dilute hydrochloric acid.

CHAPTER XV.

BARIUM, STRONTIUM, CALCIUM.

THE CARBONATE GROUP.

THE three metals of this group possess quite similar properties. They form insoluble carbonates in ammoniacal solutions, even in the presence of ammonium chlorid, which is present here to prevent the precipitation of magnesium at the same time. They form insoluble carbonates, and hence the name "carbonate group." Magnesium, through the intervention of ammonium chlorid, is placed in the next group, although it has many properties in accord with the members of this group.

The members of the carbonate group, with the exception of calcium, are not of interest pharmaceutically, for there are no official salts of barium, since barium dioxid was dropped, and strontium has but three recognized salts. There are, however, ten compounds of calcium official and many more commonly used.

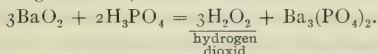
BARIUM, Ba, 137.2. Sp. gr., 4.

Barium does not occur native, and the metal is so difficult to isolate that some doubt exists as to whether strictly pure barium has ever been produced.

Its most abundant natural compounds are *heavy spar*, BaSO_4 , and *witherite*, BaCO_3 .

Barium forms two oxids, BaO and BaO_2 .

Barium dioxid, BaO_2 , is a grayish-white powder, decomposed by dilute acids, and this property has made the salt valuable in the preparation of solutions of hydrogen dioxid; thus:



Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, finds use only as a reagent and for producing "green fires" (Bengal lights).

Barium sulfid, BaS , is prepared by reducing the sulfate by heating with coal dust. The salt is soluble in water and used as depilatory.

Barium chlorid, BaCl_2 , and *barium carbonate*, BaCO_3 , find use as chemical reagents only.

Toxicology.—Soluble salts of barium are poisonous, though but few cases of poisoning with barium ever occur. Any soluble sulfate, such as sodium or magnesium sulfate, when given, form with barium, insoluble sulfates, which should be removed with emetics.

Tests.—Barium salts are readily precipitated from their solutions with soluble carbonates or sulfates, and the sulfate so formed is insoluble in acids. Chromates also produce an insoluble, primrose-yellow barium chromate; *distinction from calcium and strontium*, which form soluble chromates.

STRONTIUM, Sr, 87.3.

The principal minerals of strontium are *strontianite*, SrCO_3 , and *celestite*, SrSO_4 . These ores are found but sparingly. Strontium is found in very small

quantities in gypsum, some limestones and mineral waters.

Description.—Strontium is a yellow, lustrous metal, and resembles barium and calcium in most properties. Strontium compounds impart a red color to the flame, and the nitrate is much used in pyrotechny as the principal constituent of "red fires."

Strontium salts are not considered as poisonous except in large quantities. As stated, there are but three salts officially recognized.

Strontium bromid (strontii bromidum U. S. P.), $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$. Purity, 97%. *Description*: Colorless, transparent crystals, very deliquescent, soluble in one part of water. Used in medicine as a sedative nervine.

Strontium iodid (strontii iodidum U. S. P.), $\text{SrI}_2 + 6\text{H}_2\text{O}$, should be at least 98% pure.

Description.—Colorless, transparent plates; deliquescent and not permanent in the air. Soluble in 0.5 part of water. Used as an alterative.

Strontium salicylate (strontii salicylas U. S. P.), $\text{Sr}(\text{C}_7\text{H}_5\text{O}_3)_2 + 2\text{H}_2\text{O}$. Purity, 98.5%. White, crystalline powder, soluble in 18 parts of water. Used medicinally as an antirheumatic and antiseptic.

All the strontium salts are prepared by acting upon the carbonate or hydroxid with the respective acid solution.

Tests.—Strontium may be detected by the crimson color imparted to the flame.

With sulfuric acid, strontium salts form insoluble sulfates.

With soluble carbonates or oxalates, strontium salts give insoluble precipitates.

The precipitated sulfate is insoluble in solution of ammonium sulfate (distinction from calcium).

CALCIUM, Ca, 40. Sp. gr., 1.6.

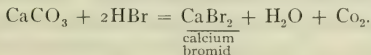
Calcium does not occur free, but is very widely distributed in its compounds. The carbonate, CaCO_3 , in *limestone*, *marble* and *chalk*, the sulfate, CaSO_4 , as *gypsum* and *alabaster*, and the phosphate, $\text{CaH}_4(\text{PO}_4)_2$, silicate, CaSiO_3 , and fluorid, CaF_2 , are most widely distributed minerals. Some of these compounds occur in most natural waters and soils and also in vegetable and animal tissues. Bones consist largely of calcium phosphate. The element was first isolated by Davy (1808), the most common means of separation now being through the electrolysis of the fused chlorid.

Properties.—Calcium is a pale, brass-yellow colored metal, hard but malleable; acted on easily by moist air, burns readily when heated in air, and decomposes water.

Compounds.—The compounds of calcium are numerous and of much value commercially as well as pharmaceutically and medicinally. Ten salts or compounds are recognized in the Pharmacopeia.

Calcium bromid (calcii bromidum U. S. P.), CaBr_2 ; 97% pure.

Preparation.—From the carbonate with hydrobromic acid. Reaction:



Very soluble. *All the other salts of calcium may be prepared in a similar way.*

Calcium hypophosphite (calcii hypophosphis, U. S. P.), $\text{Ca}(\text{PH}_2\text{O}_2)_2$; 98% pure. This is prepared by warming calcium hydroxid with phosphorus and water.

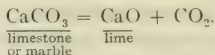
In preparing this salt great care must be used, as phosphin, PH_3 , a highly explosive gas is formed, and good draughts are necessary to carry it off. The temperature employed should not exceed 85°C .

$$4\text{P}_2 + 3\text{Ca}(\text{OH})_2 + 6\text{H}_2\text{O} = 3\underbrace{\text{Ca}(\text{H}_2\text{PO}_2)_2}_{\text{calcium hypophosphite}} + 2\text{PH}_3.$$

Quicklime (calx U. S. P.), CaO . Calcium oxid. Lime.

Description.—Hard, white or gray masses; soluble in 760 parts of water. In air it slowly absorbs moisture and falls to a gray powder (air-slaked lime, $\text{Ca}(\text{OH})_2$). With water this change takes place rapidly.

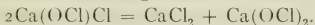
Quicklime is manufactured from limestone—native calcium carbonate, CaCO_3 —by burning in kilns (narrow furnaces, usually of brick), to remove carbon dioxid. Thus:



Lime is noncombustible, and when heated in the oxyhydrogen flame it emits a brilliant light known as the "lime light." It is much used as a drying agent on account of its affinity for water. When slaked as described, it becomes a hydroxid which is slightly soluble, and solutions of this are known as *lime*

water (liquor calcis U. S. P.) which should contain at least 0.14% of the hydroxid. The hydroxid, citrate and oxalate of calcium are more soluble in cold than in hot water. "Milk of lime" is a pasty mass of calcium hydroxid with water, made by slaking lime, the lime being in excess. Lime also enters into building mortars where its cementing property is due to the absorption of carbon dioxid from the air whereby the calcium carbonate forms.

Chlorinated Lime (calx chlorinata U. S. P.), $\text{Ca}(\text{OCl})\text{Cl}$. Bleaching powder, bleach, "chloride of lime." It should, when assayed, yield not less than 35% of available chlorin. It is prepared by the action of chlorin on slaked lime. When treated with water, the following reaction occurs:



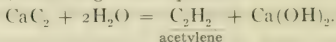
When treated with acids, chlorin is generated:



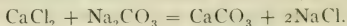
Chlorinated lime is used as a disinfectant, deodorant and as a bleaching agent. It enters into the solution of chlorinated soda, commonly called "Labarraques" (liquor sodæ chlorinatæ) which should contain at least 2.4% of available chlorin.

Sulfurated lime (calx sulphurata U. S. P.), sulfurated lime, crude calcium sulfid, is a mixture containing at least 60% calcium sulfid, with sulfate and carbon. Made by heating together 70 parts of dried calcium sulfate, 10 parts of charcoal and 2 parts of starch to redness until the mass loses its black color. Then it is pulverized and should be preserved tightly stoppered.

Calcium carbid, CaC_2 , unofficial, is prepared in an electric furnace from coal tar and lime. It decomposes in contact with water, furnishing acetylene gas, according to the equation:



Precipitated calcium carbonate (calcii carbonas precipitatus U. S. P.), CaCO_3 , precipitated chalk; purity 99%: The salt is made by precipitating calcium chlorid with a soluble carbonate, as sodium:



This is a purer salt than *prepared chalk* (creta preparata U. S. P.), CaCO_3 —a white or gray powder or moulded conical drops, made by elutriation. The prepared chalk is less crystalline and smoother than precipitated chalk, and hence is directed in preparations for internal administration.

“Paris white” and “whiting” are synonyms for the impure prepared chalk, both are used in polishing mixtures, etc.

Calcium chlorid (calcii chloridum U. S. P.), CaCl_2 ; 99% pure.

Description.—Anhydrous, white, fused masses; very deliquescent, readily soluble. Its greatest value is as a drying agent, due to its great affinity for water, which it will absorb from gases or liquids.

Precipitated calcium phosphate (calcii phosphas precipitatus, U. S. P.), $\text{Ca}_3(\text{PO}_4)_2$. Bone phosphate, normal calcium orthophosphate; purity, 99%. A permanent, white, insoluble powder. The salt occurs in the phosphate rock of Florida and South

Carolina, in which it is sometimes found up to 90%. The "precipitated phosphate" is made by adding calcium chlorid and ammonium hydroxid to phosphate, known as "white rouge."

A number of phosphates are formed with calcium, such as tricalcic phosphate, bone phosphate, dicalcium phosphate, $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$, and monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$ "superphosphate." The rock phosphate is used extensively as a valuable fertilizer.

Calcium sulfate, $\text{CaSO}_4 + 2\text{H}_2\text{O}$. Crystalline, sparingly soluble, called gypsum, selenite and "terra alba." Heated to 120°C ., it gives up its water, becomes an opaque mass, which, when ground, constitutes the official "plaster of Paris" (calcii sulfas exsiccatus, U. S. P.), CaSO_4 , "dried gypsum." The "plaster of Paris" still contains about 5% of water. When mixed with water, it reabsorbs two molecules of it and hardens to a stone-like mass. Upon this property depends the value of plaster of Paris in preparing surgical dressings, moulds, etc.

Calcium salts are not poisonous and, in fact, are found normally present in every part of the human body, in tissues, fluids of the body, etc., being most abundant in the bones and teeth—bones containing about 55% and teeth about 72% of calcium salts.

Tests. Calcium may be detected in solution by its insoluble carbonates, sulfates and especially its oxalate precipitates, which are formed with the soluble salts of the corresponding acid.

With Bunsen flame it gives a brick-red coloration.

CHAPTER XVI.

THE ALKALI-METAL GROUP.

Lithium, 7	Rubidium, 85
Sodium, 23	Cesium, 133
Potassium, 39	Ammonium, 18

We have no general reagent for the metals of this group. Each member is separated or detected individually.

Their grouping together is due to a number of characteristics, which they possess in common. Thus:

All have a low specific gravity; are monatomic; soft and easily fusible; have great affinity for oxygen and decompose water, forming hydroxids which dissolve in excess of water. These hydroxids turn red litmus blue, neutralize acids, saponify fats and, if strongly concentrated, are caustic to the point of eschar. These properties, characteristic of alkalis, give the name of "alkali metals" to the members of this group. Their great affinity for oxygen causes them to oxidize in the air, to tarnish immediately and even to take fire, due to the heat produced by the rapid oxidation. They are, therefore, kept beneath a mineral oil, free from oxygen, to prevent rapid oxidation.

Lithium, sodium and potassium were discovered in

1807-1808 by Sir Humphrey Davy, and cesium and rubidium by Kirchoff and Bunsen in 1860-1861.

The relation between the atomic weights is an interesting point. There is a difference of 16 in the atomic weight of lithium and sodium; the same between sodium and potassium; practically three times sixteen between potassium and rubidium and between rubidium and cesium. This seems to show them to lie in an homologous series, with two undiscovered metals belonging in the spaces on each side of rubidium. These metals form many salts, but only one chlorid, bromid and iodid. As a general statement, it may be said that the salts of alkali metals are white, crystalline compounds, soluble, odorless, characteristic in taste and permanent.

LITHIUM, Li, 7. Sp. gr., 0.589.

Occurrence.—Lithium occurs widely distributed, but in very small quantities, as in mineral springs, in plants, especially in tobacco and the beet. It is usually separated from its chlorid by electrolysis.

Properties.—A silver-white metal, fusible at $180^{\circ}\text{C}.$, burns with an intense red flame. It is the lightest metal of the solid elements.

Compounds.—The salts of lithium so closely resemble those of sodium as to require no separate discussion.

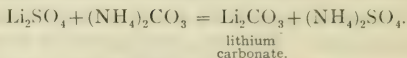
Those recognized officially are:

Lithium bromid (lithii bromidum U. S. P.), LiBr ; purity, 97%.

Used as a sedative nervine.

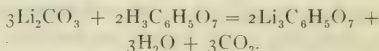
Lithium carbonate (lithii carbonas U. S. P.), Li_2CO_3 ;

purity, 98.5%. Made according to the following reaction:



Used as an alkalin diuretic.

Lithium citrate (lithii citras U. S. P.), $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 + 4\text{H}_2\text{O}$; purity, 98.5%. *Preparation* from the carbonate:



Used as a diuretic. This salt forms with uric acid a salt, which is the most soluble of all its compounds; hence the use of lithium in uric-acid poisoning. It enters into (lithii citras effervescens, 5%) the effervescent citrate.

Lithium salicylate (lithii salicylas U. S. P.), $\text{LiC}_7\text{H}_5\text{O}_3$; purity, 98.5%. Used as an antirheumatic.

Lithium benzoate, (lithii benzoas U. S. P.), $\text{LiC}_7\text{H}_5\text{O}_2$; purity, 98.5%. The salt is used as an intestinal antiseptic. • As may be readily seen, all the salts of lithium may be prepared by the action of the respective acid upon lithium carbonate. The physical characteristics of the lithium salts are so similar to those of sodium that in general the description of the corresponding sodium salt will apply to lithium as well. See later description under Sodium.

POTASSIUM, Kalium; K, 39. Sp. gr., 0.865.

Occurrence.—Widely distributed in rocks and minerals, particularly as *sylvite*, KCl, and *carnallite*, KCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; found in the mines of Stassfurt.

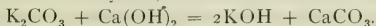
Germany, which are the principal source. Also found in plant ash, in argols (crude potassium tartrate), and in niter beds Calcutta niter, KNO_3 .

Preparation.—The metal is obtained by reduction of its carbonate by means of carbon and high heat in an iron retort and subsequent redistillation.

Properties.—It is a silver-white, lustrous metal, soft at ordinary temperature, brittle at 0°C ., fusing at 62°C . It distills at a red heat. Potassium has great affinity for oxygen, and tarnishes immediately when exposed to the air, and frequently ignites. It burns with a peculiar grayish-purple flame. It decomposes water, liberating hydrogen gas. Must be preserved under a hydrocarbon oil, as kerosene.

Compounds.—The salts of potassium are very numerous and very common, many quite similar to the corresponding sodium salt, which can be seen for comparison. There are eighteen compounds of potassium recognized in the U. S. P.

Potassium hydroxid (potassii hydroxidum U. S. P.), KOH . (Potassa U. S. P. '90); potassium hydrate, caustic potash. Made by the action of slaked lime on potassium carbonate. The solution is decanted, evaporated to dryness, fused and cast into moulds:



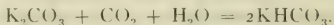
Purity, 85%, and not more than 2% of other inorganic substances, with the exception of water. White, hard pencils, very soluble in water and in alcohol. With fats, mixed oils and resins it forms soaps. Uses: caustic and solvent. Preparations: liq. potassii hydroxidi, 5%.

Vienna lime (potassa cum calce), not official. Made by fusing together equal parts of KOH and CaO.

Potassium acetate (potassii acetat), $\text{KC}_2\text{H}_3\text{O}_2$. Purity 98%. A white powder or crystalline masses, saline taste; very deliquescent. Made by decomposing potassium bicarbonate with acetic acid, filtering and evaporating.

$\text{KHCO}_3 + \text{CH}_3\text{COOH} = \text{CH}_3\text{COOK} + \text{CO}_2 + \text{H}_2\text{O}$. Soluble in 0.4 part water, 2 parts alcohol. Precipitates strong solutions of quinine salts; effervesces with spirits of nitrous ether. Alkaline diuretic.

Potassium bicarbonate (potassii bicarbonas), KHCO_3 . Should contain not less than 99% of pure salt. Colorless, transparent crystals or colorless, odorless, granular powder, saline, alkaline taste. Prepared by passing CO_2 in a solution of a carbonate, evaporating and crystallizing. Antacid. Soluble in 3 parts water, almost insoluble in alcohol.

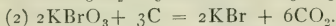


Also called "saleratus" or "baking salt."

Potassium bitartrate (potassii bitartras), $\text{KHC}_4\text{H}_4\text{O}_6$. Cream of tartar. Purity, 99%. Colorless, slightly opaque crystals or white, gritty powder. Odorless, with pleasant, acidulous taste. Made by purifying "argol," the sediment deposited during fermentation of wine in barrels. Soluble in 200 parts water, more soluble in solutions of borax or boric acid, sparingly soluble in alcohol. With hydroxids and carbonates of the alkalis it forms soluble neutral salts. Used as a diuretic and cathartic. As cathar-

tic, it is often prescribed with sulfur and administered with molasses and water. *Impurity*: Calcium tartrate; forming white precipitate with ammonium oxalate.

Potassium bromid (potassii bromidum U. S. P.), KBr. Purity, 97%. Colorless, in cubical crystals or a granular powder. Odorless, possessing a strong saline taste. Made by treating solution of potassium hydroxid with bromin, evaporating and igniting with charcoal. In the reaction both the bromid and bromate are formed. When heated with charcoal and starch, the bromate is deoxidized, CO_2 escaping. Thus:

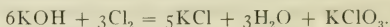


Potassium carbonate (potassii carbonas U. S. P.), K_2CO_3 . *Sal tartar*, pearlash. Should contain when thoroughly dried not less than 98% of the pure salt. A white, granular powder, odorless, strongly alkaline taste, very deliquescent. Made by purifying common pearlash by dissolving it in *cold* water, filtering, evaporating and granulating. Carbonates are decomposed by acids, excepting hydrocyanic. Both potassium and sodium carbonates precipitate salt solutions of nearly all other common metals. Free alkaloids are precipitated from their aqueous salt solution by the carbonates.

Lye, potash and "pearlash" are produced when ashes from burnt wood are lixiviated or "leached" (percolated) with water. The percolate is evaporated in iron pots, and the impure carbonate is

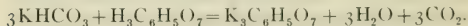
called "pearlash," "potash" or "lye". Soluble in 1 part of water. Poisonous.

Potassium chlorate (potassii chloras), KClO_3 . Kali chloricum. Purity, 99%. Made by passing chlorine gas into a solution of potassium hydroxid and boiling, according to the following reaction:



Also prepared by reacting on potassium chlorid with calcium hypochlorite solution. Soluble in 16 parts water. Chlorates are powerful oxidizing agents, incompatible with reducing agents, with which they explode on dry trituration or heating. When triturated with organic substances, as tannic acid, cork or sugar, or with inorganic substances, as sulfur, antimony sulfid, phosphorus or other easily oxidizable substances, it conflagrates. *Description*: Colorless, lustrous prisms or plates or a white granular powder; odorless; cooling taste. Used as antiseptic, stimulant to mucous membrane. Preparations: Troche, KClO_3 (0.15 gm. in each).

Potassium citrate (potassii citras U. S. P.), $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$. Purity, 99%. Prepared by neutralizing solutions of citric acid with potassium bicarbonate, evaporating and granulating:



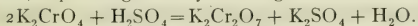
Transparent crystals or white, granular powder, deliquescent, odorless, with a cooling taste. Soluble in 0.5 part water, sparingly in alcohol. Incompatible with lead and silver salts, lime water, and quinine solutions. Used as alkalin diuretic. Prep-

arations: *Potassii citras effervescens*, 20%; *liquor potassii citras*, 8%.

In the *Pharmacopœia*, 1880, *mistura potassii citratæ* was official, known as "neutral mixture." This was a more agreeable preparation to the taste, made by nearly neutralizing lemon-juice with potassium bicarbonate.

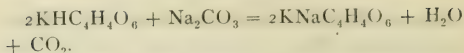
Potassium cyanid (*potassii cyanidum* U. S. P.), KCN. "Poisonous prussiate of potash." White, opaque, amorphous pieces or granular powder; odorless when dry; deliquescent in air, emitting the odor of HCN. Soluble in 2 parts water, sparingly in alcohol.

Potassium dichromate (*potassii dichromas* U. S. P.), $K_2Cr_2O_7$, known in the last *Pharmacopœia* as "*potassii bichromas*." Bichromate of potash. Purity, 99%. *Description*: Large, orange-red, transparent prisms or tabular crystals, odorless, acid, metallic taste. Made by treating potassium chromate with sulfuric acid, evaporating and crystallizing. Thus:



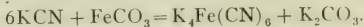
A powerful oxidizing agent, almost universally incompatible. Soluble in 9 parts water. Insoluble in alcohol. Used as caustic and antiseptic in pills or capsules, with kaolin as diluent and petrolatum as excipient.

Potassium sodium tartrate (*potassii et sodii tartras* U. S. P.), $KNaC_4H_4O_6 + 4H_2O$. Rochelle salts, Seignettes salts. Colorless, transparent prisms or white powder. Odorless, cooling taste, efflorescent. Purity, 99%. Made by treating solution of potassium bitartrate with sodium carbonate.



Soluble in 1.2 parts water. Insoluble in alcohol. Incompatible with nearly all acids. Used as hydrogogue purgative. Preparations: (Pulv. Efferv. Comp.) Seidlitz powder.

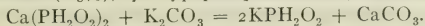
Potassium ferrocyanid (potassii ferrocyanidum U. S. P.), $\text{K}_4\text{Fe(CN)}_6 + 3\text{H}_2\text{O}$. Yellow prussiate of potash. Large, soft, transparent, yellow, four-sided crystals or prisms. Odorless, with mild, saline taste. Slightly efflorescent. Purity, 99%. Made by treating nitrogenized substances (refuse animal matter, such as hair, hoofs, horns, etc.) with crude potash, with which impure potassium cyanid is formed. This mass is lixiviated and treated with freshly precipitated ferrous carbonate, with which the ferrocyanid is formed. Thus:



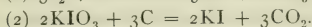
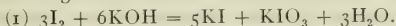
Soluble in 4 parts water; insoluble in alcohol. Used mainly in the preparation of cyanids. (Potassii ferricyanidum), $\text{K}_3\text{Fe(CN)}_6$, • "Red prussiate of potash. Not official. Employed as reagent for the detection of ferrous salts, with which it gives blue precipitates.

Potassium Hypophosphite (potassii hypophosphis U. S. P.), KPH_2O_2 . Purity, 98%. Should be preserved in well-stoppered bottles. White, opaque, hexagonal plates or crystalline masses or granular powder. *Description*: Odorless, pungent, saline taste, very deliquescent. Made by precipitating calcium hypophosphite with potassium carbonate,

filtering, evaporating and granulating at a temperature below 100°C . Above this degree of heat, the salt explodes. Explosions have occurred when this salt was triturated or heated with nitrates, chlorates or other oxidizable substances. Solubility: 0.5 part water, 7 of alcohol. Insoluble in ether. Used as expectorant tonic. Preparations: Syr. hypophosphitum (1.5%), Syr. hypophosphitum comp. (1.75%).



Potassium iodid (potassii iodidum U. S. P.), KI. Made by adding iodine to hot solution of KOH, evaporating to dryness, mixing with charcoal or starch, heating to redness, dissolving in water and crystallizing.



The charcoal or starch is added to convert the oxygen into CO_2 , and thus reduce the iodate and convert it into an iodid. *Description:* Colorless, transparent, translucent or opaque, white cubical crystals or a white granular salt, with faint, iodine-like odor, pungent, saline, afterward bitter taste. Purity, 99%. Slightly deliquescent in moist air. The commercial salt is crystallized from an alkaline solution, making it more stable, and occurs in white crystals having an alkaline reaction, owing to the presence of potassium carbonate. The chemically-pure salt should have a neutral reaction. Soluble in 0.7 part water, 12 parts alcohol, 2.5 parts glycerin. Incompatible with lead and silver salts. Alterative. Preparation: Ung. Pot. Iodidi (10%).

Test to Detect Iodate.—Add gelatinized starch and dilute H_2SO_4 . A blue color will appear.

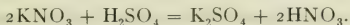
Potassium nitrate (potassii nitras U.S.P.), KNO_3 . Saltpeter, niter, Calcutta niter. Purity, 99%. Found native in India. *Description:* Colorless, transparent crystals or white, crystalline powder. Odorless, with a cooling, saline taste. Soluble in 3.6 parts water, sparingly in alcohol. Obtained by lixiviating the earth from the niter beds of India and filtering, evaporating and crystallizing. Used as a diuretic.

Potassium permanganate (potassii permanganas U. S. P.), KMnO_4 . Purity, 99%. Comes in slender, monoclinic prisms of a dark purple color and a blue metallic luster by reflected light. Odorless; taste at first sweet, afterward disagreeable and astringent. Used as antiseptic, deodorant, emmenagogue. Administered in pill form with kaolin and petrolatum. Made by boiling a solution of potassium manganate with water.

$$3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} = 2\text{KMnO}_4 + \text{MnO}_2 + 4\text{KOH}.$$
Soluble in 15 parts of water; it decomposes in contact with alcohol or glycerin. It is a powerful oxidizing agent, very incompatible with reducing agents, with some of which it explodes on dry trituration. It should not be brought in contact with organic substances.

Potassium sulfate (potassii sulphas U. S. P.), K_2SO_4 . Purity, 99%. Hard, colorless, transparent crystals or a white powder, odorless, having a somewhat bitter, saline taste. Soluble in 9 parts water, insoluble in alcohol. Used as cathartic. Made by

purifying residue from nitric acid manufacture. Native as kainite. Found in the Stassfurt salt beds as a double sulfate of potassium and magnesium. Made directly by decomposing common niter with H_2SO_4 , thus:

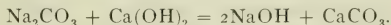


Among the frequently used compounds of potash. is *potassa sulphurata*—sulfurated potash (liver of sulfur). Made by heating together sublimed sulfur, 1, and potassium carbonate, 2.

SODIUM, Na, 23.

Sources: (1) *Sea water*; (2) mineral springs; (3) *cryolite*, the double fluorid of sodium and aluminum; (4) *borax lakes* of California; (5) *Chili niter*. The salts of sodium are cheaper and more frequently used than those of potassium. As a rule, they are also more soluble.

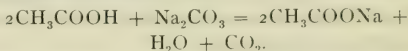
Sodium hydroxid (sodii hydroxidum), NaOH . Caustic soda, sodium hydrate. Known in the last U. S. P. as “soda.” Prepared from slaked lime and sodium carbonate. The solution is decanted and evaporated. The crude salt is largely contaminated with carbonate and called “soda ash.”



Purity, 90%, and not more than 2% of other inorganic substances. *Description*: Dry, white flakes, fused masses or sticks. Soluble in 1 part water. Very soluble in alcohol. With salts it forms acids and water. Preparations: Liq. sodii hydroxidi (5%). Antacid. The chemically-pure salt is prepared by

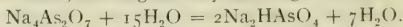
oxidizing metallic sodium with distilled water and evaporating.

Sodium acetate (sodii acetas U. S. P.), $\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}$. *Description*: Large, colorless, transparent, monoclinic prisms or granular powder, efflorescent, odorless, bitter taste, alkaline reaction. Purity, 99.5%. Made by decomposing sodium carbonate with acetic acid.



Sodium acetate is soluble in 1 part water, 23 parts alcohol. Used as diuretic.

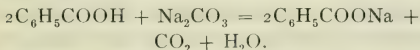
Sodium arsenate (sodii arsenas), $\text{Na}_2\text{HAsO}_4 + 7\text{H}_2\text{O}$. Purity, 98% of pure disodium-orthoarsenate. *Description*: Colorless, transparent crystals, having a mild, alkaline taste. Very poisonous; soluble in 1.2 parts water, sparingly in alcohol; precipitated by tannic acid. Oxidizes hypophosphites, sulfites and iodides. Precipitates alkaloidal salts. Used as tonic, alterative, hematinic. Made by heating together arsenous acid, sodium nitrate and carbonate, which form sodium pyroarsenate. The pyroarsenate is then converted into the orthoarsenate by dissolving it in water, filtering and crystallizing. Thus:



Exsiccated sodium arsenate (sodii arsenas exsiccatus) should contain not less than 98% of anhydrous disodium-orthoarsenate. Prepared by drying the crystals at a temperature between 40 and 50° C. until disintegrated, then at 150° C. until they cease to lose weight. *Description*: An amorphous white

powder, odorless, and having a mild, alkalin taste. Preparations: Liq. sodii arsenatis (1%).

Sodium Benzoate (sodii benzoas), C_6H_5COONa . Purity, 99%. *Description*: A white, amorphous, granular or crystalline powder; odorless with a sweetish, astringent taste. Soluble in 1.6 parts water, 43 parts alcohol. Stronger acids precipitate it from its solution. It precipitates also salts of silver, mercury and lead; precipitates pinkish ferric benzoate from the neutral chlorid and solutions of quinine bisulfate. Used as antiseptic, expectorant, diuretic. Made by decomposing sodium carbonate with benzoic acid.



Sodium bicarbonate (sodii bicarbonas), $NaHCO_3$. Purity, 99%. *Description*: A white, opaque, powder, odorless with a cooling, mildly alkalin taste. Also called "baking soda" and *soda saleratus*. Made by washing commercial $NaHCO_3$ with H_2O . *Solvay's process*:



Preparation: Troch. sodii bicarb. Solubility: 12 parts water.

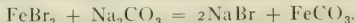
Sodium bisulfite (sodii bisulphis), $NaHSO_3$. Purity, 90%. *Description*: Opaque, prismatic crystals or granular powder with odor of SO_2 and a disagreeable sulfurous taste. Exposed to the air, it is gradually oxidized to a sulfate. Made by saturating sodium carbonate with sulfurous acid.

$$Na_2CO_3 + 2H_2SO_3 = 2NaHSO_3 + CO_2 + H_2O.$$

Soluble in 3.5 parts water, 70 parts alcohol. Incompatible with acids. Antiseptic.

Sodium borate (sodii boras), $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$. Borax. Purity not less than 99% of pure sodium tetraborate (orthoborate). *Description*: Colorless crystals or a white powder, having a sweetish, alkaline taste. Soluble in 20.4 parts water, 1 part glycerin; insoluble in alcohol. Incompatible with neutral solutions of many metals. Also with alum, calcium chlorid and barium chlorid. With mineral acids, boric acid is precipitated out. It precipitates alkaloidal salts; glycerin, glucose or honey liberate boric acid from solutions of borax, rendering them incompatible with carbonates. Mild antiseptic. Made by purifying the neutral salts found as a crystalline deposit in the blue mud of Clear Lake, California. It is also called *tincal*. Found in Tuscany as crude boric acid.

Sodium bromid (sodii bromidum U. S. P.), NaBr . Purity, when dried, 97%. *Description*: Colorless or white cubical crystals or granular powder, saline, with bitter taste. Absorbs water from the air without deliquescing. Soluble in 1.7 parts water, 12.5 parts alcohol. Incompatible with alkaloidal salt solutions. Made by treating ferrous bromid with sodium carbonate, filtering, evaporating and crystallizing.



Used as sedative nervine.

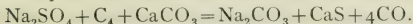
Monohydrated sodium carbonate (sodii carbonas monohydratus U. S. P.), $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$. Purity, 85% of pure anhydrous salt, corresponding to 99.5%

of the crystallized salt. *Description:* Monohydrated sodium carbonate is a white, crystalline, granular powder, odorless, with strong alkalin taste. It effloresces at 50 C., and at 100° C. loses its water of crystallization (14.5%). *Leblanc's process:* Common salt is converted into the carbonate by two steps:

1st step: into the sulfate:



2d step: the sulfate with charcoal into carbonate:



This mass is now digested in warm water which dissolves out the alkali, leaving behind the insoluble "soda waste," which latter is used in the manufacture of sodium hyposulfite. The above solution is evaporated to dryness and the mass calcined with sawdust, which converts the alkali, owing to its CO_2 , fully into carbonate. This is redissolved, filtered and evaporated. This "soda ash" contains about 50% of sodium carbonate. The Cryolite process is used in the United States: *Cryolite*, a double fluorid of aluminum and sodium ($\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$) is heated with chalk. The mass is leached by lixiviation. The alumina becomes insoluble and is deposited. The liquid is filtered, purified and crystallized. In the U. S. P. '90, *sodii carbonas* was official, a salt which contained ten molecules of water of crystallization. This has been supplanted with the monohydrated sodium carbonate. *Sodii carbonas exsiccat* (dried) was also official. Used as antacid. Solubility: 2.9 parts water, 8 parts glycerin, insoluble in alcohol and ether.

Sodium chlorate (sodii chloras U. S. P.), NaClO_3 . Purity, 99%. Colorless, transparent crystals or a crystalline powder; odorless, cooling saline taste. Soluble in 1 part water, 5 parts glycerin, 100 parts alcohol.

Caution: Sodium chlorate is explosive when heated or triturated with organic substances or oxidizable bodies. Made by the *Wittstein process*, from sodium carbonate and tartaric acid.

$\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{C}_4\text{H}_4\text{O}_6 = 2\text{NaHC}_4\text{H}_4\text{O}_6 + \text{CO}_2 + \text{H}_2\text{O}$. Then the bitartrate is added to potassium chlorate.

$\text{NaHC}_4\text{H}_4\text{O}_6 + \text{KClO}_3 = \text{NaClO}_3 + \text{KHC}_4\text{H}_4\text{O}_6$.

Note.—When this salt is prescribed, under no circumstances should *sodium chlorid* be dispensed.

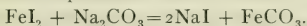
Sodium chlorid (sodii chloridum), NaCl . Sal communis, sal culinaris, common salt. Purity, when dried, 99%. *Description:* colorless, transparent cubical crystals or a white, crystalline powder. Permanent in dry air, pure saline taste, obtained by evaporating sea-water and the brine from salt wells and springs. When magnesium chlorid is present as impurity, the salt is very deliquescent.

Sodium citrate (sodii citras), $2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 11\text{H}_2\text{O}$. Purity, 97%. A white, odorless, granular powder, having a cooling, saline taste. Effloresces slowly. Prepared by adding sodium carbonate to a solution of citric acid until effervescence ceases, evaporating and granulating. Soluble in 1.1 parts water, slightly in alcohol. Diuretic.

Sodium hypophosphite (sodii hypophosphis), $\text{NaPH}_2\text{O}_2 + \text{H}_2\text{O}$. Purity, 98%. *Description:* Small,

colorless, transparent plates of pearly luster or white granular powder. Odorless, bitterish, saline taste. *Very deliquescent*. Made by double decomposition between calcium hypophosphite and sodium carbonate. (See reaction under potassium hypophosphite.) The salt explodes with violence during evaporation which should, therefore, be performed below 100° —better at 85° C. Soluble in 1 part water, 25 parts alcohol; insoluble in ether. Used as tonic. Preparations: Syr. hypophosphitum (1.5%) and syr. hypophos. comp. (1.75%).

Sodium iodid (sodii iodidum), NaI. Purity, 98%. Colorless, cubical crystals or crystalline powder. *Description*: Odorless, with saline, bitterish taste. Soluble in 0.5 part water, 3 parts alcohol. In moist air the salt decomposes, assuming a brown tint. Alterative. Preparation:



Insoluble iron carbonate is filtered off. The solution is then evaporated and crystallized.

Sodium nitrate (sodii nitras), NaNO_3 . Chili saltpeter, cubic niter. Purity, 99%. Found native in Chili and Peru. Obtained by lixiviation, evaporation and crystallization. Colorless, transparent, rhombohedral crystals, odorless, cooling, saline, bitterish taste. Hygroscopic. Soluble in 1.1 parts water and 100 parts alcohol. Diuretic. *This salt constitutes the cheapest source for obtaining nitrates.*

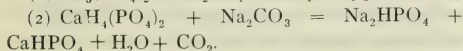
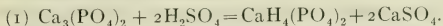
Sodium nitrite (sodii nitris), NaNO_2 . Should contain not less than 90% of the pure salt. *Descrip-*

tion: White, opaque fused masses or pencils or transparent, hexagonal crystals. Odorless, mild saline taste. Very deliquescent; gradually oxidizes and is converted into sodium nitrate and becomes unfit for use. Soluble in 1.4 parts water, slightly in alcohol. Incompatible with hypophosphites, sulfites, iodids, ammonium bromid. It reduces chlorates, permanganates, chromates, hydrogen dioxid, mercurous and mercuric salts. Vasodilator.

Sodium phenol-sulfonate (sodii phenol-sulphonas), $\text{NaC}_6\text{H}_5\text{SO}_4 + \text{H}_2\text{O}$. Purity, 99% of pure sodium parphenol-sulfonate. *Description*: Colorless, transparent, rhombic prisms, made by dissolving sodium carbonate in phenol-sulfuric acid. Soluble in 4.8 parts water, 130 parts alcohol. Antiseptic.

Sodium phosphate (sodii phosphas), $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$. Purity, in the uneffloresced condition, 99% of pure disodium-orthophosphate. *Description*: Large, colorless prisms or granular salt. Odorless, cooling, saline taste. Crystals effloresce in the air, losing 5 molecules (25%) of their water of crystallization. Cholagogue. Soluble in 5.5 parts water. The salt contains 60.3% of water of crystallization. It precipitates nearly all other metals, some of the alkaloidal salts, and liquefies when triturated with lead acetate, phenol, chloral hydrate or salicylic acid. Prepared by dissolving calcined bones (neutral calcium phosphate) in concentrated sulfuric acid. Acid calcium phosphate is formed. By boiling this solution with sodium carbonate the phosphoric acid is

completely saturated and the calcium is thrown down as insoluble calcium sulfate.



The calcium phosphate is separated by filtration and the filtrate evaporated and crystallized.

Exsiccated sodium phosphate (sodii phosphas exsiccatus). Purity, 99% of pure anhydrous salt.

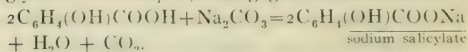
Description: A white powder which absorbs moisture readily. Made by allowing crystalline sodium phosphate to effloresce for several days in warm air at between 25 to 30° C., then drying in an oven at 100° C. until constant weight.

(Sodii phosphas effervescens) effervescent sodium phosphate is made from the exsiccated sodium phosphate—20%.

Sodium pyrophosphate (sodii pyrophosphas), $\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$. Purity, 99%. *Description:* Colorless, transparent prisms or crystalline powder. Odorless, with cooling, feebly alkaline taste. Slightly efflorescent. Made by heating sodium phosphate to redness, dissolving and crystallizing. Soluble in 11.5 parts water; insoluble in alcohol. It precipitates solutions of metallic salts. Used in the preparation of ferric pyrophosphate.

Sodium salicylate (sodii salicylas) $\text{C}_6\text{H}_4(\text{OH})\text{:COONa}$. Purity, 99.5%. *Description:* White, microcrystalline powder or scales or an amorphous, colorless powder, having not more than a faint, pink tinge. Odorless, sweetish, saline taste. Sol-

uble in 0.8 part water, 5.5 parts alcohol, also in glycerin. Antiseptic, cholagogue, antirheumatic.



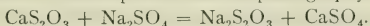
For internal administration only the salt prepared from oil of wintergreen should be dispensed.

Sodium sulfate (sodii sulphas), $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$. Glauber's salt. Purity, in the uneffloresced condition, 99%. *Description*: Large, colorless, transparent prisms or granular crystals. Odorless, saline, bitter taste. The salt effloresces rapidly in the air and quickly loses all of its water of crystallization. Made by decomposing common salt with sulfuric acid. Soluble in 2.8 parts water, also in glycerin; insoluble in alcohol. When heated, it dissolves in its own water of crystallization. Incompatible with metallic chlorids. Used as hydragogue cathartic.

Sodium sulfite (sodii sulphis), $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$. Purity, in the uneffloresced and air-dried condition, 96%. *Description*: Colorless, transparent, monoclinic prisms, odorless, cooling, saline and sulfurous taste, effloresces on exposure, and slowly oxidizes to a sulfate. Soluble in 2 parts water, sparingly in alcohol. It is decomposed by acids. Used as antiseptic. The salt is made by passing SO_2 gas into a solution of sodium carbonate, thus forming sodium bisulfite, mixing this with an equal weight of sodium carbonate, neutral sulfite is formed. $\text{Na}_2\text{CO}_3 + \text{SO}_2 = \text{Na}_2\text{SO}_3 + \text{CO}_2$.

Sodium thiosulfate (sodii thiosulphas), $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ (sodii hyposulphis U. S. P. '90) "hyposul-

fite." Purity, 98%. *Description*: Colorless, transparent, monoclinic prisms. Permanent below 33° C., but efflorescent above that temperature. Deliquescent in moist air; odorless; cooling, somewhat bitter taste, neutral reaction. Made by decomposing calcium thiosulfate with sodium sulfate. Soluble in 0.35 part water, slightly in oil of turpentine; insoluble in alcohol. Incompatible with acids; precipitates barium, silver, lead and mercurous salts from aqueous solutions. In acid solution it is a powerful reducer, incompatible with oxidizing agents. The trituration of it with strong oxidizing substances results in explosion. Antiseptic. Used in photography.

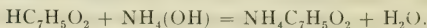


AMMONIUM, NH_4 , 18.

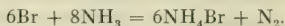
Source.—Coal-gas liquor, which is the by-product in the manufacture of boneblack. Ammonium (NH_4) is a compound of nitrogen and hydrogen. It is not found free and has never been isolated. It is a *radical*, also called a "quassi metal" and classed with the alkalis for convenience only. Ammonia (NH_3) is a saturated compound capable of existing in the free state. It occurs in the atmosphere, in natural waters and in the earth. Difference between the salts of the alkalis and ammonium is but one: all ammonium salts are volatile at a moderate temperature, the other alkali salts are not. Remember the difference between (NH_3), a *saturated compound*, and ammonium, a *radical* (NH_4). In ammonia the nitrogen is a *triad*; in ammonium it is a *pentad*.

Compounds:

Ammonium benzoate (ammonii benzoas), $\text{NH}_4\text{C}_7\text{H}_5\text{O}_2$. Purity, 98%. *Description:* Thin, white, liminar crystals or powder; odorless; saline, bitter, slightly acid taste. Soluble in 10.5 parts water, 25 parts alcohol. Used as antiseptic, expectorant, diuretic. Made by dissolving benzoic acid in ammonia water.



Ammonium bromid (ammonii bromidum), NH_4Br . Purity, 97%. Should be preserved in well-stoppered bottles. Colorless, prismatic crystals or crystalline powder; odorless, with pungent, salty taste. Soluble in 1.2 parts water; 12.5 parts alcohol. Sedative nervine. Made by *Pile's process* of adding ammonia water to bromine water:



Ammonium carbonate (ammonii carbonas), $\text{C}_2\text{H}_{11}\text{N}_3\text{O}_5$. Should contain not less than 97% of a mixture of ammonium bicarbonate and ammonium carbamate, and should yield not less than 31.58% of ammonia gas. For dispensing purposes, only the translucent portions should be used. The opaque, friable white powder or porous lumps on the outside are the inert ammonium bicarbonate, and should be rejected. Also known as "baker's ammonia," *sal volatile*, *hartshorn*. *Description:* White, hard, translucent masses, with strong ammoniacal odor and a sharp saline taste. Changes to white powder on exposure to the air. Soluble in 4 parts water; alcohol dissolves the carbamate, but not the bicarbonate.

When the official salt is dissolved in water containing ammonia gas, it is converted into the *true carbonate*, the formula for which is $(\text{NH}_4)_2\text{CO}_3$, according to the following reactions:

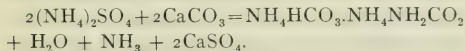
From the carbamate:



From the bicarbonate:



The salt is made by subliming a mixture of ammonium sulfate and calcium carbonate:



Used as a reflex stimulant, carminative, expectorant. Preparations: *Liquor ammonii acetatis* (5%). Incompatible with mercuric chlorid, calomel, copper and silver salts, alkaloidal salts. It should be dispensed with care with syrups of squills, ipecac and of citric acid or any syrup containing an acid.

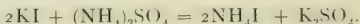
Ammonium chlorid (*ammonii chloridum*), NH_4Cl . *Sal ammoniac*, *muriate of ammonia*, *battery ammonia*. Purity, 99.5%. *Description*: White crystalline powder, permanent, odorless, cooling, saline taste, with a neutral reaction. Soluble in 2 parts water, 50 parts alcohol and 5 parts glycerin, and 1 part boiling water. Made by subliming a mixture of ammonium sulfate (a by-product from gas manufacture) and sodium chlorid.



Incompatible with alkali hydrates or carbonates or the hydroxids of the earthy metals which liberate NH_3 gas from it. With chlorin gas explosive

nitrogen chlorid may be formed. Expectorant, hepatic stimulant. Preparations: Troch. ammonii chloridi (0.1 gm. each).

Ammonium iodid (ammonii iodidum), NH_4I . Purity, 97%. When deeply colored, the salt should not be dispensed. It may be deprived of free iodine by adding to its concentrated solution ammonium sulfid sufficient to decolorize it, filtering, evaporating on water-bath to dryness. *Description*: Minute, cubical crystals or white, granular powder; when colorless without odor, but emitting odor of iodine when colored. Sharp, saline taste, very hygroscopic. Made by mixing solutions of potassium iodid and ammonium sulfate.



Soluble in 0.6 part water, 9 parts alcohol. Alterative.

Ammonium salicylate (ammonii salicylas), $\text{NH}_4\text{C}_7\text{H}_5\text{O}_3$. Purity, 98%. Should be protected from heat and light and preserved in well-stoppered bottles. *Description*: Colorless, lustrous crystals or plates or crystalline powder. Odorless, with a slightly saline, bitter taste, and a sweetish after-taste. Made by neutralizing ammonia water with salicylic acid, evaporating and crystallizing. Soluble in 0.9 part water, 2.3 parts alcohol. Used as antiseptic, cholagogue and antirheumatic.

Ammonium valerate (ammonii valerias), $\text{NH}_4\text{C}_5\text{H}_9\text{O}_2$. (Ammonii valerianas U. S. P. '90.) *Description*: Colorless or white, quadrangular plates, emitting the odor of valeric acid, with a sharp, sweetish taste; deliquescent in moist air. Purity,

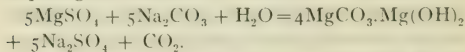
98%. Should be preserved in stoppered bottles. Made by passing ammonia gas into valerianic acid. The salt, as found in commerce, is generally the acid salt and should be neutralized with ammonia when used in solution for making preparations like the various elixirs. Very soluble in water and in alcohol; also soluble in ether. Incompatible with hydroxids and carbonates and sulfuric acid. Antispasmodic.

It should be noted that *Ammonia* combines with acids and the halogens to form corresponding salts. Ammonium iodid is readily decomposed into *nitrogen iodid*, which is *very explosive*. Ammonia water precipitates solutions of mercury, lead, silver, copper, zinc, bismuth, iron, manganese, aluminum, chromium, antimony. With mercurous chlorid it forms a black precipitate. It also precipitates tartaric and picric acid solutions. With the latter acid it forms the powerfully explosive ammonium picrate. Ammonia precipitates nearly all alkaloids from their salt solutions. It decomposes chloral into chloroform and a formate. When boiled with solutions of formaldehyd, hexamethylenamin (urotropin) forms. Permanganates oxidize it to nitrate. Reactions: with phenol, *blue color* is slowly developed; with gallic acid, *yellow to reddish-brown* coloration; *with thymol, green color* is formed. Preparations: Aqua ammoniæ (10%), sp. gr., 0.958; aqua ammoniæ fortior (28%), sp. gr., 0.897; spiritus ammoniæ (10%); spir. ammoniæ aromaticus (ammonia water, 9%; lin. ammoniæ (ammonia water, 35%).

MAGNESIUM, Mg, 24. Sp., gr., 1.75.

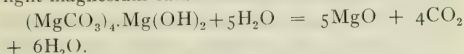
Occurrence.—Very abundant metal, not found free in nature. Many of its mineral compounds, as talc, asbestos, soapstone, magnesite, dolomite, kieserite and meerschaum, are very familiar. As a sulfate, it is found in many saline springs, as the *Epsom*, of England, and as chlorid in sea-water. The silver-white metal magnesium, in the form of a ribbon or wire, when held in a flame burns with an intensely active flame, producing a bulky, white precipitate. Four magnesium salts are official.

Magnesium carbonate (magnesii carbonas U. S. P.), $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 + 5\text{H}_2\text{O}$. When ignited, it should yield 40% of residue, of which 96% should be pure magnesium oxid. Light, white friable masses or a bulky powder; odorless with an earthy taste; permanent. Made by double decomposition between magnesium sulfate and sodium carbonate. When the solutions are made in boiling hot water, the heavy carbonate results. When the cold solutions are employed the light carbonate is the product. Insoluble in water and alcohol; dissolves in dilute acids with effervescence. Antacid, laxative. Preparations: Liq. magnesii citratis.



Magnesium oxid (magnesii oxidum U. S. P.), MgO. *Magnesia* (magnesia U. S. P. '90), calcined magnesia, light magnesia, magnesia levis). Purity: after ignition, it should yield 96% of pure magnesium oxid, a white, very bulky and very fine powder,

slowly absorbing moisture and CO_2 from the air. Odorless, with earthy taste. Made by calcining light magnesium carbonate.



Almost insoluble in water; dissolves in acids. With 15 times its weight of water it gelatinizes forming a hydrate. Antacid.

Heavy magnesium oxid (magnesii oxidum ponderosum U. S. P.), MgO (magnesia ponderosa U. S. P. '90), heavy magnesia. A white, dense and very fine powder which should conform to the reactions and tests given under magnesii oxidum. It differs from the latter in not readily uniting with water to form a gelatinous hydroxid. The salt is similar to the light magnesia, except in possessing only one-fourth the bulk which facilitates its administration. It is prepared by calcining *heavy* magnesium carbonate which is produced by precipitating a hot, concentrated solution of magnesium sulfate with sodium carbonate. The salt is soluble in acids; insoluble in water and alcohol. Used as antacid and laxative.

Magnesium sulfate (magnesii sulphas), $\text{MgSO}_4 + 7\text{H}_2\text{O}$, commonly called Epsom salt, after the English spring in which it is found. It is also manufactured from the mineral kieserite, which is an impure sulfate containing but one molecule of water of crystallization. Four-sided prisms or acicular crystals. Odorless, cooling, saline, bitter taste. Slowly efflorescent in the air. Soluble in 0.85 part

water and in 0.13 parts hot water; insoluble in alcohol. Used for the preparation of the carbonate. Soluble magnesium salts are precipitated by soluble hydroxids and carbonates (except ammonium salts) and by phosphates, arsenates, sulfites, oxalates and tartrates; also incompatible with the chlorids of the heavy metals. Used as hydragogue purgative. Preparations: *Magnesii sulphas effervescens* (50%).

Tests.—The following method may be employed to detect the metals of this group. To a portion of the solution add sodium hydroxid and heat in a test-tube. The formation of *ammonia*, which may be detected by its *odor* or action on test papers or white fumes with hydrochloric acid prove the presence of *ammonium compounds*.

To a second portion add ammonium chlorid, ammonium hydroxid and sodium phosphate. A *white, crystalline precipitate* of ammonium magnesium phosphate proves the presence of *magnesium*.

Evaporate a third and quite a large portion of the original solution to dryness and ignite sufficiently to volatilize all ammonium salts. Dissolve the residue in a small amount of water, add a drop of hydrochloric acid. Dip a clean platinum wire formed into a small loop into the solution and place it in the Bunsen flame. An *intense yellow* color indicates *sodium*; a *lilac* or grayish-purple color shows *potassium*. Examined through a polariscope, potassium is indicated by a crimson line. Add to the solution of the above residue a few drops of platinic chlorid solution: A *yellow precipitate* of potassium

platino-chlorid *confirms potassium*. *Lithium* in solution imparts a brilliant *carmine-red* to the *flame*. Disodium phosphate boiled with the lithium solution produces an *insoluble lithium phosphate*. This precipitation is complete when sodium hydroxid is present.

CLASSIFICATION OF THE ELEMENTS ACCORDING TO "PERIODIC LAW."

As has already been noticed, the nonmetallic elements seem to arrange themselves into groups or families. The halogens, for example, obviously form a group of closely related elements; and it is found that in such a group there is a more or less regular increase in the atomic weights. Thus, the atomic weight of bromin (80) is nearly the mean between the atomic weights of chlorin and iodin.

$$\frac{35.5 + 127}{2} = 81.2$$

Carbon and silicon, oxygen and sulfur, nitrogen and phosphorus are similarly related. Among the metals, we have the group lithium, sodium and potassium; the continuation of the nitrogen family—arsenic, antimony and bismuth, etc. John Newlands (1864) pointed out that, if the elements were arranged in the numerical order of their atomic weights, there was a recurrence of similarity in chemical and physical properties at every eighth element. He called this "The Law of Octaves."

NEWLAND'S CLASSIFICATION OF THE ELEMENTS.

Atomic weight		Atomic weight	
Lithium,	7	Sodium,	23
Beryllium,	9	Magnesium,	24
Boron,	11	Aluminum,	27
Carbon,	12	Silicon,	28
Nitrogen,	14	Phosphorus,	31
Oxygen,	16	Sulfur,	32
Fluorin	19	Chlorin,	35.5

About five years afterwards this idea was worked out more fully by Mendelejeff, who published a table of the elements arranged according to his "Periodic Law," as represented on page 173.

The following points should be noticed:

(a) After the first two octaves (lithium to chlorin), the resemblance is most marked between alternate rather than between consecutive octaves; thus, taking the second vertical column, magnesium, zinc and cadmium form a natural group, and the other alternate octaves, calcium, strontium and barium, form a second natural group.

(b) After manganese, a triplet of metals occurs—iron, nickel and cobalt—forming a sort of supplementary eighth vertical column; the other triplets are ruthenium, rhodium and palladium, and osmium, iridium and platinum. The atomic weights in each of these triplets are close together; thus, Fe, 56; Co, 59; Ni, 58.3. All these metals have high melting-points.

(c) The valences of the elements may be said to increase as we pass from the first to the seventh column; thus: sodium is a monad; magnesium, a dyad; aluminum, a triad; carbon, a tetrad; nitrogen, a pentad; sulfur, a hexad; manganese, a heptad; the same fact is indicated by the formulas of the oxids at the top of the table. On the other hand, the compounds with hydrogen show a diminishing number of atoms of hydrogen in the molecule as we pass from left to right; thus, CH_4 , NH_3 , OH_2 , ClH .

Outside the great theoretical interest of this classification, it is of a practical use in several ways:

(1) As a check on the atomic weights; thus, tellurium is an element which closely resembles selenium and sulfur; its old atomic weight was 128, which would place it after iodine in a group to which it was obviously not related; recent determinations have reduced the number to 127, and it seems extremely probable that it has not been obtained perfectly pure. The atomic weight of indium is 38, and its atomic weight was at one time believed to be $38 \times 2 = 76$, but as there is no space for an element between arsenic and selenium, it was suggested that its atomic weight must be $38 \times 3 = 114$, which would place it in the column under aluminum. This number was actually confirmed by determining its specific heat.

(2) The classification enables us to prophesy the existence and properties, physical and chemical, of undiscovered elements; thus, in columns III and IV, when the table was first published the elements gallium (Ga) and germanium (Ge) were unknown,

but by comparing the properties of aluminum and indium in one case and of silicon and tin in the other, an accurate forecast of all the chief properties of these elements was made and completely verified when the elements were isolated.

There seems to be some difficulty in finding satisfactory places for the recent elements, argon, helium, neon, etc.

MENDELEJEFF'S CLASSIFICATION OF THE ELEMENTS.

I	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O	R_2O_2	R_2O_3	R_2O_4 RH_4	R_2O_5 RH_5	R_2O_6 RH_6	R_2O_7 RH_7	R_2O_8 (?)
H 1 Li 7 Na 23 K 39 63.6 Cu Rb 85 108 Ag Cs 133	Be 9 Ca 40 65.4 Zn Sr 87 112 Cd Ba 137.4	B 11 27 Al Sc 44 69 Ga Y 89 113 In La 138	C 12 28 Si Ti 48 72.5 Ge Zr 90 119 Sn Ce 140	N 14 31 P V 51 75 As Nb 94 120 Sb	O 16 32 S Cr 52 79 Se Mo 96 127 Te	F 19 35.5 Cl Mn 55 80 Br — 127 I	— — — Fe 56. Co 59. Ni 59 — Ru 102. Rh 103. Pd 106 — — — Os 191. Ir 193. Pt 195 — — —
— 197 Au —	— 200 Hg —	Yb 173 204 Tl Th 232	— 208 Bi —	Ta 183 — —	W 184 — U 239.5	— — —	— — —

CHAPTER XVII.

THE RARE METALS.

THESE metals are of such rarity or of so little value in pharmacy, as to be deemed scarcely worthy of a place in the discussion of the several groups.

I. The following are the *rare metals* of the *hydrochloric acid group*, *thallium* and *tungsten*. The group reagent precipitates them as thallos chlorid and tungstic acid.

THALLIUM, Th, 204, resembles lead in many ways and the alkali metals in some others. It is precipitated as chlorid, but this chlorid readily dissolves in sulfuric acid, forming *soluble thallos sulfate*. *Thallium compounds* impart a *brilliant green* to the flame.

TUNGSTEN, W, 184. The most commonly met with compound of tungsten is *sodium tungstate*, which is one of several compounds with sodium. Sodium metatungstate is used to render fabrics unflammable.

Tungsten compounds are characterized by the *blue color* given when *metallic zinc* is added to its solution and the solution strongly acidified with *hydrochloric acid*.

The rare metals of group II or the hydrogen sulfid group.

I. **GOLD**, Au, 197, and **PLATINUM**, Pt, 194. These metals are really not rare metals, since they are so well known in a general way, but it is not often

that the pharmacy student is called upon to consider compounds containing them. Usually they are met with only as alloys. These metals are insoluble in acids, except the nitrohydrochloric which yields their chlorids. Because of their solubility in this acid it received the name "aqua regia" (kingwater). These metals together with silver and mercury are classed as the "noble metals." But few simple salts are known and these are characterized by the ease with which they are reduced to the metallic state. The chlorids of these metals are precipitated by hydrogen sulfid or ammonium sulfid, forming sulfids; on boiling the solution the gold comes down in the metallic state. Both gold and platinum form double salts with the alkaline chlorids; thus NaCl-AuCl_3 ; NaClPtCl_4 . Stannous chlorid with a gold solution gives a reddish-brown to purple color or precipitate, known as the "purple of Cassius."

II. Four rare elements—*Iridium*, *tellurium*, *selenium* and *molybdenum* form sulfids with the group reagent H_2S . They are soluble in ammonium sulfid, hence belong to the arsenic division.

IRIDIUM, Ir, 193.1, differs from platinum in *not* being *soluble in aqua regia*. In general it resembles platinum.

TELLURIUM, Te, 25 (1) and **SELENIUM**, Se, 78.8, are on the border-line between nonmetals and metals. They so closely resemble sulfur, as to be classed with the sulfur group.

MOLYBDENUM, Mo, 96, is usually met with as the *ammonium molybdate*, $(\text{NH}_4)_2\text{MoO}_4$, and is mostly

used to precipitate phosphorus, with which it forms the yellow, insoluble ammonium phosphomolybdate.

Ruthenium, Ru, 101.6; *Rhodium*, Rh, 103; *Palladium*, Pd, 106.5, and *Osmium*, Os, 190.8. These four elements belong to the platinum group—their sulfids are insoluble in ammonium sulfid. The first two are seldom met with, palladium and osmium more frequently. Osmium, forming osmic acid, is used in the preparation of microscopic sections of animal tissues. This compound is really a tetroxid, OsO_4 , or an anhydrid. The rare elements of the ammonium sulfid group may be divided for convenience into five classes, in accordance with the form in which each is precipitated. Tabulated thus:

I.	II.	III.	IV.	V.
(a)	(a)	(a)	(a)	(a)
Beryllium	Scandium	Zirconium	Titanium	Uranium
Be, 9	Sc, 43.9	Zr, 90.4	Ti, 48	U, 230.6
$\text{Be}(\text{OH})_2$	$\text{Sc}(\text{OH})_3$	$\text{Zr}(\text{OH})_4$	H_2TiO_3	UO_2S
	(b)	(b)	(b)	(b)
	Yttrium	Thorium	Tantalum	Indium
	Y, 89.1	Th, 232	Ta, 182.6	In, 113.7
	$\text{Y}(\text{OH})_3$	$\text{Th}(\text{OH})_4$	H_3TaO_4	InS
	(c)		(c)	(c)
	Ytterbium		Niobium	Thallium
	Yb, 173		Nb, 93.7	Th, 204.2
	$\text{Yb}(\text{OH})_3$		H_3NbO_4	Th_2S
	(d)			(d)
	Cerium			Vanadium
	Ce, 133			V, 51
	$\text{Ce}(\text{OH})_3$			Not pre-
	(e)			cipitated
	Lanthanum			
	La, 138.2			
	$\text{La}(\text{OH})_3$			

Uses.—These rare elements do not as yet find much application in the arts.

Zirconium is used in the manufacture of the so-called “Welsbach gas mantles,” where it assists in the “incandescence.”

Uranium is used as a chemical reagent.

Uranium acetate finds considerable application in the volumetric estimation of phosphates.

Cerium is found in many minerals, but especially in cerite—a silicate. Cerium oxalate is its important medicinal salt, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 + 9\text{H}_2\text{O}$. Made by precipitating cerous chlorid with ammonium oxalate. The official cerium oxalate is not a pure salt, but is a mixture of the oxalates of cerium, didymium, lanthanum and other rare earths.

The rare elements of the alkalin group comprise *Rubidium*, Rb, 85.3, and *Cesium*, Cs, 132.6. These possess almost identical characteristics with potassium and can be detected only with difficulty. Their separation is based upon the comparative solubility of their chloro-platinates. They play no special part in ordinary chemistry or pharmacy.

VALENCES OF THE METALS.

Sym- bol		Valence in "ous" com- pounds	Valence in "ic" com- pounds	Atomic weights
Ag	Silver.....	1	1	107.1
Pb	Lead.....	2	2	205.3
Hg'	Mercury (ous).....	1	...	198.3
As	Arsenic.....	3	5	74.4
Sb	Antimony.....	3	5	119.3
Sn	Tin.....	2	4	118.1
Bi	Bismuth.....	3	5	206.9
Cu	Copper.....	1	2	63.1
Hg''	Mercury (ic).....	...	2	198.3
Cd	Cadmium.....	...	2	111.6
Fe	Iron.....	2	3	55.5
Co	Cobalt.....	2	3	58.5
Ni	Nickel.....	2	3	58.3
Mn	Manganese.....	2	3	54.6
Zn	Zinc.....	...	2	64.9
Al	Aluminum.....	...	3	26.9
Cr	Chromium.....	2	3, 4, 6	51.7
Ca	Calcium.....	...	2	39.8
Sr	Strontium.....	...	2	86.9
Ba	Barium.....	...	2	136.4
Mg	Magnesium.....	...	2	24.1
Li	Lithium.....	...	1	6.9
Na	Sodium.....	...	1	22.8
K	Potassium.....	...	1	38.8
(NH ₄)'	Ammonium.....	...	1	18

THE IONIC THEORY.—When solutions are subjected to the action of an electric current, a decomposition known as electrolysis takes place, and the minute particles separated, called "ions," are attracted to the *positive pole*, called the electric *anode*, and to the *negative pole*, called the *cathode*. The *ions* attracted to the *anode*, positive pole, are electro-

positive (+), and are called *anions*. Those collecting at the *negative pole* (—), or *cathode*, are *electro-negative*, and called *cathions*. As a general rule, the metallic elements form positive ions and the non-metallic, negative ions. The positive ions attract the negative ions and repel the positive, the inverse being true for the negative ions. The *polarity of an ion* may, however, be changed by the inducing action of other ions.

Valence.—By analysis of a great number of hydrogen compounds, it has been determined that different elements combine with it in definite proportions, but that these proportions vary in different compounds and with different elements. It was found that chlorine unites with hydrogen in proportion to its atomic weight. Thus: 35.4 parts by weight of chlorine unite with 1 part by weight of hydrogen. But oxygen unites in half its atomic weight, or requires two atoms of hydrogen to one atom of oxygen. Nitrogen similarly requires three atoms of hydrogen; carbon, four atoms, etc. This power of combination is known as valence, and the valence of any element depends upon the number of atoms of hydrogen or its equivalent that the element will unite with or replace in a compound.

PHYSICAL CHEMISTRY AND ELECTRO-CHEMISTRY.

At the present time two distinctive and very important branches of chemistry are receiving much consideration and study; these are *physical chemistry*

and *electrochemistry*. These branches make use of the physical constants to determine the characteristics, properties, etc., of any element or compound. Close study is made of the effects of heat and cold, light, color, pressure, temperature and their changes, polarimetric properties, etc., are all taken into account. In *electrochemistry* the distinctive properties of the electric current are made use of and applied in the arts. Thus, union among the gases may readily be brought about by the action of an induction spark.

By passing the galvanic current, however, such union of gas may again be resolved into its constituents. We can, therefore, employ the electric current for both synthesis and analysis. Decomposition of compounds by electric current is called *electrolytic*; the operation, *electrolysis*. Thus, a solution of zinc sulfate may be electrolyzed according to the following equation: $\text{ZnSO}_4 + (\text{electric current}) = \text{Zn (at cathode)} + \text{SO}_4 \text{ (at anode)}$. The electropositive metallic zinc is deposited at the negative pole (cathode) and the electronegative radical (SO_4) separates at the positive pole (anode). The substance to be electrolyzed must be in a gaseous, liquid, or fused condition, and is known as *electrolyte*. The particles into which a salt will electrolyze are called "*ions*"; thus, zinc sulfate is composed of two ions—Zn and the (SO_4) radical.

Application of the electric current is made use of in *chemical analysis* for depositing the metals, which can be done quantitatively, and in *electrotyping*—or depositing of a layer of copper over moulds or type—

for the purpose of reproducing the same. Electrotypes are made use of in the printing of books, magazines, maps, etc., and are made from the forms set up by the printer. Such electrotypes can be preserved for subsequent use.

Electroplating is the process of depositing electrolytically one metal upon another—usually a cheaper one.

Electricity is also used in the *refining of metals*, preparation of *caustic alkalis, chlorates, hypochlorites, white lead, Prussian blue, etc.*, also many *organic compounds*.

CHAPTER XVIII.

CHEMICAL NOMENCLATURE AND CHEMICAL FORMULAS.

BERZELIUS (1815) proposed the short-hand form of chemical language; since that time, we are employing a system of symbols and symbolic formulas for the elements and compounds.

In Chapter II simple definitions were given for the acids, salts, etc. It is difficult—almost impossible—to give concise definitions in chemistry.

BASE is a term properly applied to a combination of a basic oxid with water, thus, $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$, called sodium hydroxid, hydrate, or simply soda; $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$, called calcium hydroxid, hydrate, etc., are bases.

Sodium oxid, Na_2O , calcium oxid, CaO , are incorrectly termed *bases*.

ACID (1) is a compound of an electronegative element or radical with *hydrogen*, part or all of which can be exchanged for an electropositive element without forming a base. (2) An acid is a salt of hydrogen. An acid can be produced by combining an anhydrid with water; thus, $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3 =$ nitric acid. Elements like S, Cl, Br, I, etc., combine with hydrogen directly, forming acids; thus, sulfur produces $\text{H}_2\text{S} =$ hydrosulfuric acid; iodine produces $\text{HI} =$ hydriodic acid, etc.

SALT is hard to define concisely: (1) Salt is an acid in which the hydrogen has been replaced either in part or entirely by a metal or radical. (2) Salt is a combination of an anhydrid with a basic oxid; thus, $\text{Na}_2\text{O} + \text{N}_2\text{O}_5 = 2\text{NaNO}_3$. Salts may be *normal*, *acid* or *basic*.

ANHYDRID is an *acid oxid*. It is the part of an acid remaining after the removal of the elements of water. Anhydrids combine with water to form acids.

$2\text{HNO}_3 - \text{H}_2\text{O} = \text{N}_2\text{O}_5 =$ nitric (oxid) anhydrid.

nitric acid

$\text{H}_2\text{SO}_4 - \text{H}_2\text{O} = \text{SO}_3 =$ sulfuric (oxid) anhydrid.

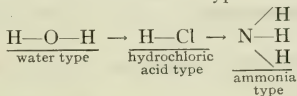
sulfuric acid

With water these anhydrids re-form the acid: $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 =$ sulfuric acid.

EMPIRIC FORMULA is the expression of the simplest ratio of the elements composing a compound. Thus, FeO_3H_3 is the empiric formula for ferric hydroxid, and CH_2O , the empiric formula for acetic acid.

MOLECULAR FORMULA is the expression of the actual number of atoms of each element in a molecule. It may be identical with the empiric formula or a multiple of it; thus, $\text{C}_2\text{H}_4\text{O}_2$ is the molecular formula for acetic acid.

TYPE FORMULA is a molecular formula arranged after one of the three common types:



ISOMERISM is a term designating bodies having

the same empiric formulas but different properties. Isomerism applies to compounds, while to elements is applied the term—

ALLOTROPISM, a term designating those modifications of an element which present different physical properties. Thus, phosphorus exists in two modifications: the yellow, which is inflammable and poisonous, and the red, which is noninflammable and nonpoisonous. Carbon exists in three allotropic forms: diamond, graphite and coal.

POLYMERISM applies to compounds having the same empiric but different molecular formulas; thus, aldehyd has the formula C_2H_4O ; its *polymer* paraldehyd has the formula $C_6H_{12}O_3$; it is derived by multiplying the aldehyd formula by 3.

HOMOLOGOUS SERIES is a group of substances with similar properties, whose molecular weights have a common difference; thus, the paraffin series differ by CH_2 group from one another and by 14 in their molecular weights.

ISOLOGOUS SERIES in organic chemistry applies to substances differing by H_2 ; thus:

C_2H_6 = ethane; C_2H_4 = ethylene; C_2H_2 = acetylene, are isologous compounds.

AMORPHOUS is applied to bodies incapable of crystallization.

MONOMORPHOUS, capable of crystallizing in one form.

DIMORPHOUS, crystallizing in two forms, as sulfur.

TRIMORPHOUS and **POLYMORPHOUS** are terms

applied to bodies crystallizing in three forms and many forms, respectively.

ISOMORPHOUS is a term applied to different bodies crystallizing in the same form.

ALLOY is a mixture of two or more metals.

AMALGAM is a term applied to the union of a metal with mercury. (Hg does not amalgamate Fe or P.)

EFFLORESCENT substances are those which lose their water of crystallization at ordinary temperatures (Na_2CO_3).

DELIQUESCENT substances are those which absorb sufficient water from air to form a solution at ordinary temperatures (KOH).

CLASSIFICATION OF THE ELEMENTS ACCORDING TO VALENCE.

Those having one bond— (monads)	With 2 bonds (dyads)	With 3 bonds (triads)	With 4 bonds (tetrads)	With 5 bonds (pentads)	With 6 bonds (hexads)
Hydrogen Chlorin Bromin Iodin Fluorin Potassium Cerium Lithium Silver	Oxygen Barium Calcium Strontium Magnesium Copper Zinc Mercury Cadmium Sulfur Chromium Manganese Carbon Iron (ous) Lead Tin (ous)	Aluminum Boron Iron Gold Bismuth Nitrogen Phosphorus Arsenic Antimony	Carbon Silicon Tin Platinum Sulfur Chromium Manganese	Nitrogen Phosphorus Arsenic Antimony	Sulfur Chromium Manganese

EQUATION WRITING.

A Study of Chemical Changes.

Under certain conditions all material bodies may undergo certain changes. When these changes occur within the molecular structure of these bodies, they may be said to be "chemical changes." Thus, when two bodies upon coming in contact exert an action on one another, such action is called a *reaction*. A body which when added to another body causes such a change is called a *reagent*; the *results of the reaction* are called *products*, and the *reactive* bodies are termed *factors*.

Thus, when metallic zinc is brought in contact with sulfuric acid, zinc sulfate is formed and hydrogen gas is given off. Thus, zinc is the reactive body, H_2SO_4 the reagent, zinc sulfate and hydrogen gas are the products, while zinc and the acid have served as the factors in the reaction.

Equations are representations of chemical reactions by means of symbols and algebraic signs.

In writing equations, the symbolic formulas of the factors, united by the plus sign (+) are written to the *left* of the equality sign (=), while the symbolic formulas of the products, also united by the plus (+) sign, are written to the *right* of the equality sign.

The reaction between zinc and sulfuric acid is illustrated by the following equation:



In another chapter it has been stated that *symbols represent definite weights*. Equations can therefore be easily reduced to figures. Thus, atomic weights of the elements entering in the above equation are zinc = 65; H_2SO_4 equals H = 2, S = 32, O = 16.

We had, therefore, 65 parts of zinc reacting with 98 parts of sulfuric acid, which produced 161 parts of zinc sulfate and 2 parts of hydrogen. If we examine further into this reaction, we will see that the total atomic weight of the factors to the left of the sign of equality is 163, and that those of the product to the right is found to be the same. In a correctly written equation the sum-total of the atomic weights on both sides of the sign of equality must balance and so must the number of atoms on each side. The following should be remembered while constructing equations:

(1) That *positive atoms* unite only with *negatives*, and not with *positives*.

(2) That the *valences* of the atoms and radicals *must* in all cases *be satisfied* (saturated).

(3) That the *members* of an equation *must represent whole molecules*.

(4) That *compound radicals* usually *remain as such* in the *products*.

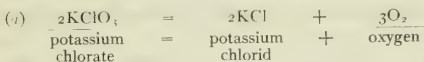
(5) That *acids* and *bases* neutralize each other and therefore cannot exist in the same solution.

(6) That an equation *must balance* before it can be regarded as completely representing a chemical change.

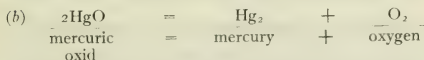
A thorough knowledge of the rules of writing chemical equations is of absolute importance, and the student should pay most careful attention to them. By the method of presentation given below the student can quickly grasp the gist of the subject. The simpler equations are discussed first, followed by the more complex and difficult ones.

Equations may be divided into four classes:

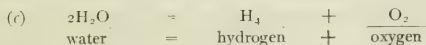
(1) *Analytic Equations.*—Under this heading are included those equations which represent the splitting of more complex compounds into simpler ones. Thus, when potassium *chlorate* is heated, it splits up into potassium *chlorid* and *oxygen*. This can serve as a typical equation representing analysis (from *ana*, up; *lysis*, separation):



Mercuric oxid splits into mercury and oxygen:

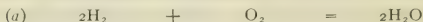


By means of electricity, water can be decomposed into its elements—hydrogen and oxygen:

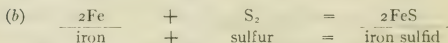


(2) *Synthetic Equations.*—Under this head belong equations representing the union of elements to form compounds, also the union of simpler compounds to form more complex ones. A type of *synthetic* (from *syn*, together; *thesis*, bringing)

reaction is the following, which represents the formation of water from its elements:



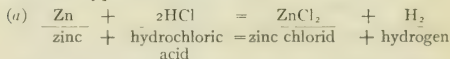
The formation of iron sulfid from its elements:



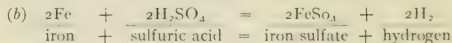
The formation of sulfur dioxide in the process of burning sulfur in the air; the sulfur vapor combining with the oxygen of the air:



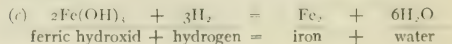
(3) *Single Decomposition Equations.*—Under this heading are included those reactions in which one of the factors is split, the other remaining intact. The *action* of *hydrochloric acid* on *zinc*, in which the acid splits into its elements (hydrogen and chlorin), serves as a *type*:



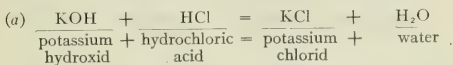
When dilute sulfuric acid acts on iron, iron sulfate (ferrous sulfate) is formed and hydrogen is set free. (The iron sulfate may be called a *product*, while the *hydrogen* in such operation is usually termed a *by-product*.)



When iron hydroxid is heated in a stream of hydrogen, reduced iron (ferrum reductum U. S. P.) is formed:



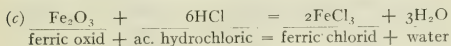
(4) *Double Decomposition Equations.*—Under this heading belong those equations in which both the factors suffer decomposition. Thus, in the action of *hydrochloric acid* on *potassium hydroxid*, *potassium chlorid* and *water* are formed, showing that both the acid and the potash were decomposed. The following may serve as a *type* for the *fourth class*.



When hydrochloric acid acts on zinc oxid, zinc chlorid and water are formed:



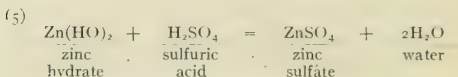
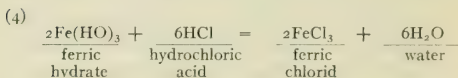
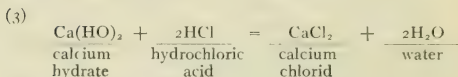
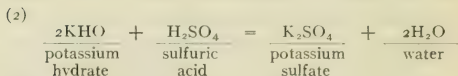
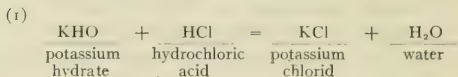
When hydrochloric acid acts on ferric oxid, ferric chlorid and water are formed:



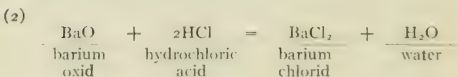
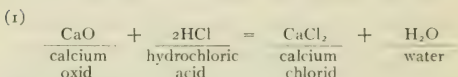
Rules for writing Equations.—All of the commoner equations belong to one of the four classes just discussed. The *seven rules* following embrace all of the reactions common to *pharmaceutic procedure*. It will be observed that most of the reactions belong to the fourth class (double decomposition). Students will do well to memorize these rules correctly, and frequently practice equation writing. Equation writing is of inestimable value in quickly grasping chemical changes and theories.

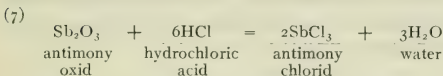
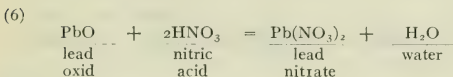
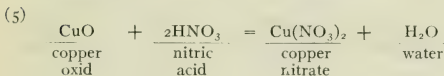
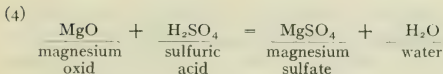
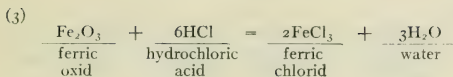
Rule I.—*Whenever a hydroxid of a metal is dis-*

solved in an acid, a salt of the metal and water are produced; thus:

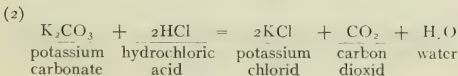
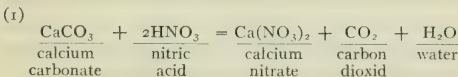


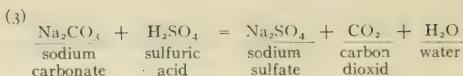
Rule II.—*Whenever an oxid of a metal is dissolved in an acid, a salt of the metal and water are produced (the only exceptions being the higher oxids of the metals); thus:*



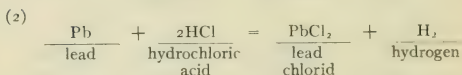
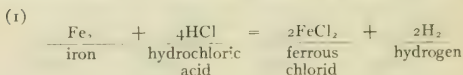


Rule III.—Whenever a carbonate of a metal is dissolved in an acid, a salt of the metal, water and carbon dioxid (carbonic-acid gas) are produced, the latter is given off. In equations the radical of the carbonates (CO_3) splits up into CO_2 and O, the former escaping, the latter uniting with the H_2 to form water; thus:

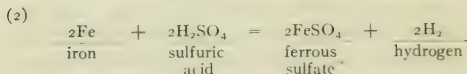
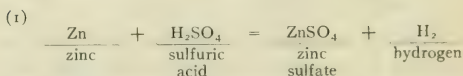




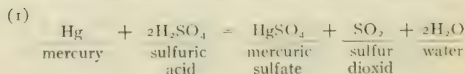
Rule IV.—*Whenever a metal is dissolved in hydrochloric acid or in aqua regia, a chlorid of the metal is always formed and hydrogen given off; thus:*

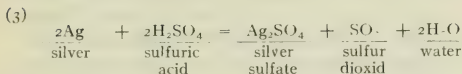
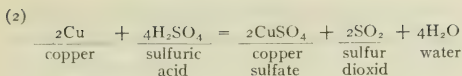


Rule V.—*Whenever a metal is dissolved in dilute sulfuric acid, a sulfate of the metal is always formed and hydrogen given off; thus:*



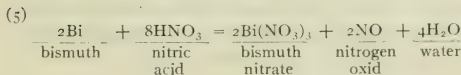
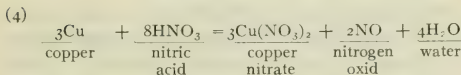
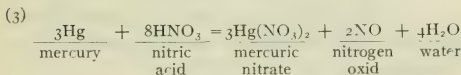
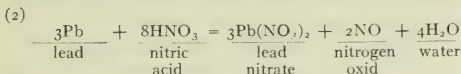
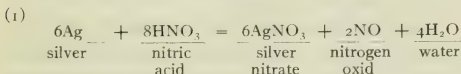
Rule VI.—*Whenever a metal is dissolved in strong sulfuric acid, a sulfate of the metal and water are formed, gaseous sulfur dioxide (SO₂) evolved. The sulfates usually made by the action of strong sulfuric acid on the metals are mercury, copper and silver sulfates; thus:*





It should be noticed that twice the required quantity of the acid is taken to furnish SO_4 for the sulfate, the extra SO_4 splitting up into SO_2 and O_2 . The former escapes and the latter unites with the hydrogen to form water.

Rule VII.—*The ordinary metals (excepting tin, antimony, arsenic and zinc), when acted upon with slightly diluted nitric acid, form metallic nitrates and evolve nitric oxid (NO); thus:*

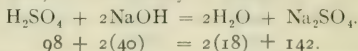


It should be noticed that *eight equivalents of nitric acid* are employed for every *six equivalents of the metal*. This is true of all the reactions of HNO_3 upon the metals; the by-products always being 2 molecules of nitric oxide and 4 of water.

STOICHIOMETRY.—It is often necessary to consider, by means of figures, the relation of the atoms in a molecule, or of molecules in a compound; also to determine percentage composition, the weight of certain volumes, etc. For this purpose *stoichiometry*, or “chemical arithmetic,” is made use of. All calculations in which use can be made of atomic weights and volumes are included in this class.

As stated, every element has its atomic weight, and every molecule and compound, therefore, has its value expressible in figures.

As already shown, all chemical changes take place between definite amounts of substance, and a chemical equation expresses the amount of matter taking part in it; thus, a reaction may be written:



The lower figures of the equation represent the quantities that take part in the reaction and express molecular weights.

The percentage of any molecule or atoms may be easily determined by comparing the quantity of the one desired with the total, on the basis of 100. Thus, in our reaction just stated, if the amount of sodium sulfate produced is desired in percentage, the proportion would be $142 : 178 :: x : 100$.

The same process of calculation would give us any factor; thus, if the percentage of sodium as an element were desired, the proportion becomes

$$2(23) : 178 :: x : 100.$$

Any other modification may be readily deduced. Care must be taken that the proper atomic weight, or multiple of it, be used in both reagent and product.

In the example given, two molecules of sodium hydrate were required to form one molecule of sodium sulfate, and twice the atomic weight of sodium entered into both factors.

If the problem had been, how much sodium sulfate would be obtained from 10 grams of sodium hydrate, the proportion would remain the same, substituting 10 for 100. The answer would then be in grams instead of in per cent.

Exactly the same calculation is employed with a single molecule as in equations; thus, if the amount of sodium present in 10 grams of sodium sulfate were desired, the proportion would be

$$\text{Na}_2\text{SO}_4 = \text{Na}_2 + \text{S} + \text{O}_4, \text{ or } (46 + 32 + 64) \\ 46 : 142 :: x : 10, \text{ etc.}$$

Modifications of this may be readily deduced.

If volumes instead of weights came into the problem, the proportion is still the same, but each molecular formula represents two volumes, since, as previously stated, molecular weight is twice that of density, which, in turn, represents but one, and by considering each molecule as twice that stated, direct calculation may be made. Example: How much carbon dioxid can be made by burning one

liter of carbon monoxid? The reaction $(\text{CO})_2 + \text{O}_2 = (\text{CO}_2)_2$ read 4 vol. $(\text{CO}) + 2$ vol. $(\text{O}_2) = 4$ vol. (CO_2) and $4:4::1:x$. $x = 1$. 1 liter of CO_2 produced.

If the relation of weight to volume or *vice versa* is desired, divide the weight of the gas by its weight per liter, the quotient will be the number of liters; or multiplying the number of liters by the weight per liter gives the weight of the given volume. The original weight or volume is determined as stated in the last two proportions respectively. Influence of temperature and pressure on gas volumes enter the calculations:

According to Boyle's law, the volume of any gas varies inversely as the pressure, and its density directly as the pressure; hence, gas volume changes with the barometric pressure. Normal barometric pressure is 760 mm. of mercury, the factor being, therefore, 760.

Similarly, all gases vary directly as the temperature. Absolute zero is taken as -273°C ., and it is claimed, therefore, that a gas volume increases $\frac{1}{273}$ of its volume for each degree increase in temperature above 0°C . In order to correct a gas volume, therefore, to standard conditions, the following procedure may be followed: The formula

$$V' = \frac{V P}{760 \times 1 + (.00366t)},$$

in which V' =desired volume; V =stated volume; P =barometric reading; 760 = normal barometric reading; 1 = normal temperature, and .00366 = factor $\frac{1}{273}$; t =stated temperature, is used:

Example: What would be the normal volume of a gas whose volume, at 42° C. and with barometric reading 732, was 976 cubic centimeters?

Substituting in the formula we have:

$$V = \frac{976 \times 732}{760 \times 1 + (.00366 \times 42)} = \frac{714432}{876.827}.$$

Ans. = 814.7 c.c. at 0° C.

Modifications of this may be easily deduced by transposition of factors. Very many other uses may be made of stoichiometry and mathematics in chemistry, but a full discussion would require a volume in itself, and those given are but the foundation for many others.

PHARMACEUTIC CHEMISTRY.

PART II.

ORGANIC CHEMISTRY.

CHAPTER XIX.

INTRODUCTION.

THE compounds of carbon with other elements, such as hydrogen and oxygen, are so numerous that it is necessary to devote to them a special part of the study of chemistry, namely, "organic chemistry." Berzelius (1818) defined organic chemistry as the chemistry of bodies formed under the influence of life. When, however, Woehler, in 1828, in an endeavor to evaporate an aqueous solution of ammonium cyanate, found the residue composed of a substance different from ammonium cyanate, namely *urea*, the theory that "vital force" was necessary to produce these compounds became untenable. It was found that they could be produced synthetically in the laboratory of the chemist, and the original belief that organic substances could only be produced by animal or vegetable organism was found to be wrong, and a new definition for organic chemistry had to be sought. Liebig (1832) defined the science as the "chemistry of compound radicals." But, whereas

almost any molecule with more than two atoms may be supposed to contain a compound radical, that definition, it will be seen, is inaccurate; and, besides, there are many inorganic compounds which also contain compound radicals, thus, NH_4 , NO_3 , SO_4 , etc.

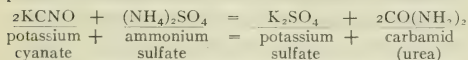
Since carbonic oxid, carbonic sulfid, carbonic acid and their salts are usually excluded from works on organic chemistry and studied in conjunction with the inorganic compounds, as containing incombustible carbon, it will be seen that the present definition is most probably correct, although by some it is claimed to be too broad.

Organic chemistry is now defined as *the study of the carbon compounds*.

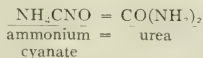
Thus, we have seen that the discovery of urea in 1828 marked the rise of true organic chemistry, and since then over one hundred thousand organic compounds have been prepared synthetically from carbon and the inorganic elements in the chemist's laboratory, duplicating many of nature's own products. It is safe to assume that every natural product will be duplicated in the laboratory, and, indeed, many which have never been detected in nature have been created there.

It may be stated that urea was not really a synthetic product, because it was only converted ammonium cyanate which, in turn was not obtained synthetically, but it has since been demonstrated over and over that this compound can be built up atom by atom from its elements. Thus, if nitrogen gas is passed over charcoal and potassium carbonate, mixed and

heated to redness, potassium cyanid is formed; and if the cyanid, in turn, is fused with lead oxid, it takes up the oxygen, becoming converted into potassium cyanate. Ammonia, on the other hand, can be formed by the direct union of nitrogen and hydrogen and absorbed by water; and if sulfuric acid be added to it, it is neutralized and converted into ammonium sulfate. If, now, the potassium cyanate and the ammonium sulfate be dissolved in water, the solution evaporated to dryness and the residue exhausted with alcohol, upon evaporation the alcohol deposits urea, the following decomposition having taken place:



Thus, we have seen urea built up atom by atom from the elements; whereas, in the discovery of Woehler, it was a simple rearrangement of the atoms in the molecule, thus:



THE SCOPE OF ORGANIC CHEMISTRY.—Until the beginning of the nineteenth century, chemistry was concerned mostly with the products of the mineral kingdom or with those of the animal and vegetable kingdoms. Those from the latter two kingdoms, which Lavoisier (1794) showed to contain carbon, hydrogen and oxygen, were called “organic” and those which were obtained from the mineral kingdom, like common salt, gypsum or water, were

called the "inorganic." But among those of the organic compounds which contained like substances, many possessed different, varying properties. Thus, sugar, vinegar and alcohol contain the same elements—carbon, hydrogen and oxygen—but their properties are very different because the elements exist there in very variable proportions. Berzelius (1814) so improved the methods of organic analysis that it was possible to make determinations of the exact composition of the organic acids and to establish the atomic ratio of the constituent elements one to another; and, although the discovery of Woehler was well known, as was the discovery of acetic acid by Melsens (1842) and Kolbe (1844), it was a long time before the belief that vital activity was necessary for the production of organic compounds, disappeared. There is a difference between an organic compound and an organism. Compounds can be created artificially, organisms cannot. For this reason it is safe to believe that the solution of the problems of life's creation is as yet afar off and the breach between the laboratory creation and that of the organism may never be mended. At least, it is far distant at the present time.

At the time of Woehler's discovery, organic chemistry embraced but a few hundred substances derived from the animal and vegetable sources. Now it contains, as has previously been stated, over one hundred thousand artificial products. This most extraordinary development can be traced directly to two principal causes: the first one was

the formulation of the laws underlying the structure of organic compounds by Kekulé, and the second, the industrial application of the organic discoveries. At the present time the contributions of organic chemistry to mankind are many and varied. Thus, foods, medicines, dyes, soaps, nitroglycerin and dynamite, paper and celluloid, perfumes, ink, artificial silk, are all organic compounds, and at the present time there seems no apparent limit to the development of the industries in which organic chemistry plays an important part.

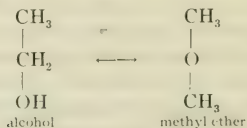
DISTINCTION BETWEEN ORGANIC AND INORGANIC CHEMISTRY.—The necessities for this division are, primarily, the large variety and complexity of organic compounds, as will be seen by the following examples:

Methane,	CH_4
Turpentine,	$\text{C}_{10}\text{H}_{16}$
Cane-sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Morphin,	$\text{C}_{17}\text{H}_{19}\text{NO}_3$
Hematin,	$\text{C}_{32}\text{H}_{32}\text{FeN}_4\text{O}_6$
Starch (soluble),	$\text{C}_{1200}\text{H}_{2000}\text{O}_{1000}$

Secondarily, owing to the different reagents and processes necessary for the production of the variety of compounds, each one requires a treatment of its own. Thus, we can oxidize iron with either nitric acid, chlorin or potassium permanganate, the result in each case being the same; not so with the organic substances where, by the employment of these different oxidizing agents, a different product would be ob-

tained in each case. Lastly, because the study of organic compounds cannot be limited to the knowledge of their components. They are very complex in structure. One who has studied inorganic chemistry will recognize at sight HNO_3 to be nitric acid and H_2SO_4 to be sulfuric acid; but to see a formula like $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, it is entirely different. Many organic substances have the same composition and molecular formula, but differ in their properties. Such substances are called *isomeric* (*isos*, equal; *meros*, part). Isomerism is a striking characteristic of many organic compounds; thus, the formula $\text{C}_8\text{H}_{12}\text{O}_4$ represents 66 different compounds. To illustrate, a familiar example is taken:

Alcohol, $\text{C}_2\text{H}_6\text{O}$, is a liquid having a boiling-point of 78° , whereas $\text{C}_2\text{H}_6\text{O}$ is also the formula of methyl ether, also called dimethyl ether, a liquid having a boiling-point of -23.6°C . This difference in the two compounds, having the same composition and molecular formula but different properties, is due to the arrangement of the atoms in the molecule. Thus, the carbon, hydrogen and oxygen are arranged in the alcohol and the methyl ether as follows:



The above substances, therefore, are isomeric, or one is an isomer of the other.

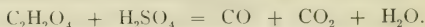
CHAPTER XX.

CARBON.

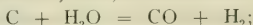
THE principal forms of carbon are: (a) *Crystalline*—the *diamond*, the purest form of all; the *graphite*, also called *plumbago* and *black lead*. Graphite is used in lead pencils, crucibles, stove polish and as a conductor of electricity in electrotyping. (b) *Amorphous*—the *anthracite*, a variety of coal composed of almost pure carbon and used as fuel; the *charcoal*, of which two varieties are used—wood and animal charcoal; the latter variety obtained by incomplete combustion of bones. Both are used as fuel, absorbents of gases, decolorizers and disinfectants. The *lampblack*, the lightest form, contains some hydrocarbons, chiefly used in printer's ink. The *gas carbon*, deposited in retorts in coal-gas manufacture, is hard and used in arc-lights and in galvanic batteries.

Combined, it is found in the form of carbonates and bicarbonates and in all organic substances, whether of vegetable or animal origin. *Properties*: All varieties of carbon are insoluble and infusible, but freely combustible (excepting carbonates and bicarbonates), burning to carbon dioxid in air. All but the diamond are good conductors of electricity. There are two oxids of carbon—CO, carbonic oxid, also called carbon monoxid, and CO₂, carbon dioxid, also called carbonic acid. Carbonic oxid is pro-

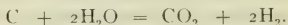
duced by the incomplete combustion of coal in the stove, or it can be made artificially by heating oxalic acid, in which case CO is given off during the decomposition, or, still, by the interaction of sulfuric acid and oxalic acid. Reaction:



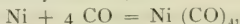
It is also produced in the manufacture of water-gas at high temperatures; thus,



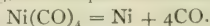
whereas, at lower temperatures CO_2 forms. Reaction:



With nickel, CO (carbonyl) forms a compound known as nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. Nickel tetracarbonyl is a liquid employed in dissolving nickel out of low-yield ores, thus:



and on heating, the compound is resolved as follows



Carbon disulfid, thiocarbonic anhydrid, $\text{C} \begin{smallmatrix} \text{S} \\ \parallel \\ \text{S} \end{smallmatrix}$, is a clear, colorless liquid, with disagreeable odor, boiling at 47°C ., sp. gr., 1.51; it forms an explosive mixture with air. Good solvent for sulfur, iodine, fats, resins and rubber.

THE NATURAL SOURCE OF CARBON.—The source of carbon compounds in nature is the carbon dioxid (CO_2) exhaled by animals into the air. It is absorbed by the leaves of plants and there, in the presence of moisture and by the agency of the sun's rays is converted by the chlorophyl (leaf-green) into

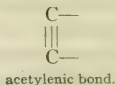
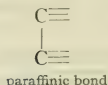
starch or similar substance. Thus, $x\text{CO}_2$ molecules + $y\text{H}_2\text{O}$ molecules = z molecules of $\text{C}_6\text{H}_{10}\text{O}_5$, or starch.

With the nitrogen of the air it forms in the plant bodies substances like the *proteins*, of which albumin is an example. These substances when ingested into the human body are decomposed into water (H_2O), carbon dioxide (CO_2), and urea ($\text{CO}(\text{NH}_2)_2$).

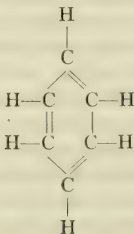
From the above it will be seen that the changes in the plant bodies are synthetic, while the changes in the human body are analytic. In the plants, energy is formed and stored; in the human body, it is evolved or expended.

Elements Entering Organic Compounds.—Carbon compounds contain few elements, but many atoms. They always contain carbon, usually hydrogen, often oxygen and nitrogen, and sometimes sulfur and phosphorus. They are very complex in structure. Thus, hemoglobin, the red coloring matter of the blood, contains in its molecule 600 atoms of carbon, 960 atoms of hydrogen, 154 of nitrogen, 179 oxygen and, in addition, 3 atoms of sulfur and 1 of iron. Whereas, in inorganic chemistry, we deal with about 85 elements, each capable of forming but a few compounds, carbon, on the other hand, is capable of forming such great multitude of compounds with so few elements, it becomes a matter of great curiosity how this can occur. The reason for it is, besides the already-mentioned isomerism, a very interesting fact, namely, that carbon can unite with itself into *chains* or *rings* to a very remarkable

degree, and around these chains or rings other atoms are attached. A *chain* is a series of multivalent atoms so combined that free bonds are left unsaturated. Thus, carbon can unite in three ways: linked by one bond and leaving six unsaturated bonds, in which case the linking is known as paraffinic; linked by two bonds, leaving four unsaturated bonds, in this case the linking being known as olefinic; and, lastly, linked by three bonds, leaving two unsaturated bonds, in which case the linking is known as acetylenic.



All the above linkings are called *open chains*. Besides these, the carbon links its atoms by alternate double and single bonds, in which case it is known as *closed chain* or ring linkage, as in the case of benzene, in which closed chain of C_6 forms a hydrocarbon having the formula C_6H_6 .



We have seen similar linkings in inorganic chemistry, as in the case of oxygen ($O = O$), and in the

case of ozone $\begin{array}{c} O \\ \diagup \quad \diagdown \\ O-O \end{array}$. The *quantivalence of carbon is always 4*.

THE CLASSIFICATION OF ORGANIC COMPOUNDS.

The immense number of substances comprising the study of organic chemistry renders classification difficult. It is primarily divided into two grand classes or divisions: (1) the methane, paraffin, fatty or marsh-gas series; (2) the benzene, ring or aromatic series. In the first class all the organic substances are considered as derivatives of methane (CH_4), and in the second class they are considered as derivatives of benzene (C_6H_6). Each of these two hydrocarbons forms a variety of derivatives which may, for convenience, be *divided into classes*:

(1) *Hydrocarbons*—compounds containing carbon and hydrogen only, as methane (CH_4), benzene (C_6H_6), naphthalene ($C_{10}H_8$).

(2) *Alcohols*—hydrocarbon radicals combined with a hydroxyl group, as ethyl alcohol (C_2H_5OH).

(3) *Aldehyds*—compounds of hydrocarbon radicals with $-CHO$ group, as acetaldehyd (CH_3CHO). They are also defined as the oxidation products of primary alcohols. (Alcohols less 2H. atoms.)

(4) *Ketones*—compounds of the divalent radical, carbonyl, $= CO$, united with two monovalent alkyl

radicals, as $\text{CH}_3\text{—CO—CH}_3$, dimethyl ketone, or acetone. (Also defined as oxidation products of secondary alcohols.)

(5) *Acids*—compounds of hydrocarbon radicals united to a carboxyl group (—COOH), as acetic acid, CH_3COOH .

(6) *Ethers*—compounds of hydrocarbon radicals with oxygen; also defined as alkyl oxids. Example, common ether, also called diethyl ether, $\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$.

(7) *Esters*—alkyl salts. They are also defined as acids in which the hydrogen of the carboxyl is replaced by an alkyl. Example, acetic ether, $\text{CH}_3\text{COOC}_2\text{H}_5$.

(8) *Carbohydrates*—compounds of carbon, with hydrogen and oxygen in the proportion to form water, as glucose, $\text{C}_6\text{H}_{12}\text{O}_6$.

(9) *Amins and Amids*: Amins are ammonias in which one, two or all three hydrogens have been replaced by alkyl groups, as methylamin, NH_2CH_3 , dimethylamin, $\text{NH}(\text{CH}_3)_2$, or trimethylamin, $\text{N}(\text{CH}_3)_3$. Amids are acids in which the OH group of the carboxyl has been replaced by the amido (NH_2) group, as acetamid, CH_3CONH_2 .

(10) *Cyanids*—compounds and derivatives of cyanogen, C_2N_2 .

(11) *Proteins*—compounds of complex structure, containing carbon, oxygen, hydrogen, nitrogen and sulfur and often phosphorus and iron, as albumin, $\text{C}_{72}\text{H}_{112}\text{N}_{18}\text{SO}_{22}$, or hemoglobin, $\text{C}_{600}\text{H}_{960}\text{N}_{154}\text{O}_{79}\text{S}_3\text{Fe}$.

(12) *Acid halids* are organic acids in which the

hydroxyl has been replaced by a halogen, as acetyl chlorid, $\text{CH}_3\text{CO.Cl}$.

(13) *Anhydrids*—acids deprived of water, as acetic anhydrid, $(\text{CH}_3\text{CO})_2\text{O}$.

(14) *Organo-metallic compounds*—alkyl compounds of the metals, as zinc ethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$.

(15) *Alkyl halids*—compounds of alkyl with halogens, as methyl iodid, CH_3I ; ethyl bromid, $\text{C}_2\text{H}_5\text{Br}$; propyl chlorid, $\text{C}_3\text{H}_7\text{Cl}$.

Another method of classification is that based on the composition and properties of many of the members of the different families of organic compounds. For instance, in the class of hydrocarbons, each member behaves toward reagents in a manner much like every other member of the same class, and the same may be said of the class of alcohols, aldehyds and ethers; but although the chemical behavior of each family is the same, the physical properties, such as specific weight, melting-points and boiling-points of the individual members, vary with each member. Thus, increased molecular weight usually shows a higher boiling-point; the *first four* members of the *paraffin* series are gases, the *next eight* are liquids, while those having the largest carbon molecule are solids.

CHAPTER XXI.

HOMOLOGY.

UPON examination of the first five members of the methane series, we find that there is a simple ratio of difference between each of the individual members. It will be observed that the ratio of difference between the members is CH_2 . It is apparent that the successive members can differ only by the same group, inasmuch as the carbon has but four valences, of which two have been satisfied by the hydrogen and two remain unsaturated. This relation is characteristic not only of the paraffin series, but also of the other hydrocarbon families. This relationship is termed *homology*, and the individual members are called homologous.

ALIPHATIC SERIES.

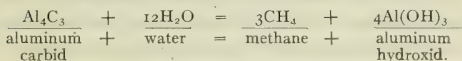
THE HYDROCARBONS.

The hydrocarbons have been defined as compounds of carbon and hydrogen only, and hence their name. They occur in nature in very large quantities and are the starting-point of a whole series of aliphatic or open-chain compounds.

Occurrence.—The hydrocarbons found in nature are almost exclusively vegetable, very few being animal products, and they are generally supposed

to be products of decomposition. Several theories have been advanced to explain their formation in nature:

First, *the chemical theory*. Based on the fact that when carbids are treated with water, hydrocarbons form; thus:



Second, *the vegetable theory, also called the theory of petroleum formation*. This depends upon the fact that when organisms act upon woody fiber (cellulose), in presence of moisture, as in the case of the decay in the stagnant pools of marshes, hydrocarbons are formed. Thus:



Third, *the biologic theory*. This theory purports that animal remains, under pressure and with sufficient water, bring about a reaction resulting in the formation of hydrocarbons. It is difficult at this stage and time to say definitely which of these three theories is the most probable. All three may be correct: paraffins may originate from either animal, vegetable or chemic matter, or all three combined.

The hydrocarbons are very important in the sense that they are looked upon as the fundamental

compounds of organic chemistry from which, directly or indirectly, all the other organic compounds are derived. They are also important, perhaps, for the reason that comparatively few of the carbon compounds do not contain hydrogen and it is, therefore, practical to consider all organic compounds as either substitution or addition products of the hydrocarbons. All the hydrocarbons, as has been stated before, are divided into series, each having a definite general formula which applies to any individual member of the entire series. Thus, the most usual classification of hydrocarbons is into the four *general classes* or *series*: (1) The methane, paraffin or chain series; (2) the ethylene or olefin series; (3) acetylene series; (4) the benzene, aromatic or ring series.

The general formula of the first, or methane series, is C_nH_{2n+2} . The general formula of the olefine series is C_nH_{2n} . The general formula of the third, or acetylene series, is C_nH_{2n-2} . The fourth, or benzene series, has the general formula of C_nH_{2n-6} .

FAMILIAR EXAMPLES OF THE HYDROCARBONS AND THEIR GENERAL PROPERTIES.

All students are acquainted with ordinary turpentine, also most of you have seen the oils of lemon peel or orange peel. Now you will recall that while the turpentine oil is a colorless, water-white liquid, the lemon oil is a straw-colored liquid, and the oil of orange peel, a still darker yellow-colored liquid.

One will also recall that the odor of turpentine is very unlike that of lemon and less like that of the orange-peel oil; and yet, *all the three substances are hydrocarbons belonging to the same series and having the same chemical formula, $C_{10}H_{16}$.* The above illustration is one of the striking examples of isomerism, each of the substances being an isomer of the other. The next familiar example of the hydrocarbons is methane, CH_4 , which is the principal constituent of our illuminating gas. The ordinary benzin, which we use for cleaning purposes and as a fuel, is chemically a mixture of two hydrocarbons—hexane, C_6H_{14} , and heptane, C_7H_{16} . The ordinary *petroleum jelly*, better known as *petrolatum* or vaselin, is nothing more nor less than a mixture of five hydrocarbons, from $C_{16}H_{34}$ to $C_{20}H_{42}$.

Properties.—The hydrocarbons are *insoluble in water*, but soluble in alcohol, ether, carbon disulfid, benzol, etc. They are generally *colorless*, frequently possessing *peculiar odor*. They exist in all three states of aggregation; thus, the *first four* of the paraffins are *gases*; the *next seven* are *liquids* and *those containing over twelve atoms of carbon* in a molecule are *solids*.

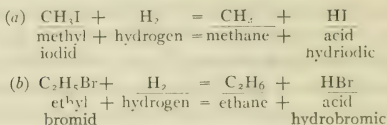
SYNTHESIS OF THE MEMBERS OF THE PARAFFIN SERIES.

There are four methods of synthesis employed:

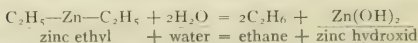
(1) *By treating alkyl halids with nascent hydrogen.*

An *alkyl halid* is a compound in which one or more

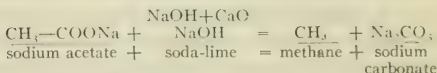
hydrogen atoms of the paraffin have been replaced by a halogen, thus:



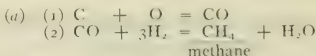
By treating any alkyl halid (iodid or bromid) with HI, the corresponding paraffin is formed. The organo-metallic compounds, like zinc ethyl, when treated with water, also yield paraffins. This latter method, however, is a dangerous one for the beginner, in that the zinc alkyls are very inflammable, even in contact with air:



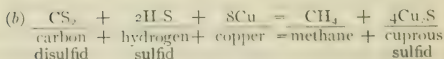
(2) *By treating an ethereal salt with alkali hydroxids or soda-lime:*



(3) *By uniting the elements:*

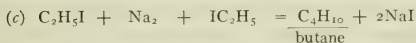
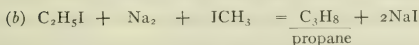
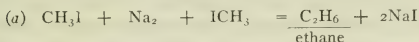


or



There is also an electrolytic method of synthesizing paraffins.

Obtaining Higher Paraffins.—By treating the alkyl halids with metallic sodium, higher paraffins of the series may be obtained:



COMPOSITION OF METHANE.

Methane has the composition CH_4 . It is a gas having the molecular weight of 16, and it is most commonly known as “marsh gas,” because when a rod is pushed into a stagnant pool on the marshes a gas bubbles out, which ignites. From this fact of the discovery of methane upon the marshes, the term “marsh-gas series” has been applied to the paraffins. The gas is also commonly found in the coal mines where it is known as fire-damp, and where it has caused many and very disastrous explosions owing to its inflammability. The origin of both marsh-gas and fire-damp is without a doubt similar, and dependent upon the action of micro-organisms on cellulose. This fact has been demon-

strated even in the laboratory where filter paper, which chemically is cellulose, under the influence of the microorganisms most common to sewage, was converted into a decomposition product and gave rise to the formation of methane. Methane has also been found in the crevices of rocks covered with limestone or shale, where it exists under a high pressure. When such a rock is bored, great quantities of gas will escape, which in Pennsylvania, Indiana and other States has proved a very economic source of fuel under the name of *natural gas*.

Specific Properties.—The characteristic properties of methane apply to every member of the series; thus, all the paraffins are very stable; they all resist the action of reagents markedly, with the exception of chlorine gas. Their boiling-points rise 30 degrees for every CH_2 group added, and their molecular weights increase by 14 criths for every CH_2 group. They are all saturated compounds and cannot directly unite with elements or residues, but indirectly form compounds after the removal of part or all of their hydrogen. Such compounds are known as *substitution* products. These substitution products are very numerous. From the above discussion it will be seen that a thorough study of the derivatives of one hydrocarbon will apply to the derivatives of all the other hydrocarbons.

The appended table of hydrocarbons of the paraffin series should be studied very carefully by the student, and their formulas, molecular weights, boiling or melting-points noticed.

TABLE OF THE PARAFFINS.

General Formula— C_nH_{2n+2}

Name.	Formula.	Boiling point.	Melting point.	Specific gravity.
Methane	CH_4	-152	-186	
Ethane	C_2H_6	-90		
Propane	C_3H_8	-37		
Butane	C_4H_{10}	+ 1		0.60 - 0° C.
Methyl propane }		-11.5		
Pentane	C_5H_{12}	36		0.633 -15° C.
Methyl butane }		31		0.627 -15° C.
Dimethyl propane }		9	-20	
Hexane	C_6H_{14}	69		0.6654 -15° C.
Dimethylisopropylmethane }		58		0.668 -17° C.
Dimethylpropylmethane }		62		0.676 - 0° C.
Methyldiethylmethane }		64		0.676 -20° C.
Trimethylethylmethane }		48		0.648 -20° C.
Heptane	C_7H_{16}	98.4		0.688 -15° C.
Isoheptane }		90		0.697 - 0° C.
Ethylpentane }		95		0.689 -27° C.
Dimethylpentane }		87		0.711 - 0° C.
Octane	C_8H_{18}	125		0.718 - 0° C.
Nonane	C_9H_{20}	150		0.733 - 0° C.
Decane	$C_{10}H_{22}$	173		0.745 - 0° C.
Undecane	$C_{11}H_{24}$	195		0.774 - 0° C.
Dodecane	$C_{12}H_{26}$	214		0.773
Eicosane	$C_{20}H_{42}$	205	37	0.778
Hentriacontane	$C_{31}H_{64}$	302	68	0.781
Pentatriacontane	$C_{35}H_{72}$	331	75	0.782

THE PETROLEUM INDUSTRY.

All of these hydrocarbons are found present in petroleum, of which some of the lower members have been isolated, but the higher paraffins are very difficult to isolate. The paraffins are likewise found associated in smaller quantities in natural gas, in asphaltum and in earth-wax (ozokerite).

Petroleum was discovered in Pennsylvania by Colonel Drake in 1860, and from that time the petroleum industry dates. Since that time oil has been found in Indiana, Ohio, Colorado, California, Texas, Canada and other places, from which the oil is distributed by means of so-called "pipe lines" to distances of more than three hundred miles. The reservoirs holding the crude oil and covered by impervious lime or shale rock, when punctured, emit petroleum to the surface by hydrostatic pressure of the water found within the crevices, which forces the oil out in enormous quantities. Crude petroleum flows from one to fifty thousand barrels from one well per day. The crude oil is not always uniform in composition; thus, in the Russian petroleum oil found in the neighborhood of the Caspian Sea, and in that found in Polish Galicia, naphthalenes are found. Crude oil is subjected to fractional distillation in large iron stills and purified by treatment with chemicals. The Russian oil contains less of the lower boiling fractions than the American oil, and its composition may be stated to be as follows: illuminating oil, 30%; lubricating oil, 20%; and solar oil (a heavy oil used for fuel), 35%; coke and inorganic substances, 15%. The American oil, on the other hand, consists of over 50% of the lighter fractions and considerably smaller proportions of lubricating oil and paraffins. When subjected to fractional distillation it is first separated into three main fractions:

The first fraction up to 150° C. constitutes crude

benzin; the second fraction up to 300° C. constitutes kerosene; and the third fraction above 300° C. constitutes the paraffin oil, paraffin wax and coke. The first two fractions are further separated by the "crack" method of distilling lighter oils. This method, however, should be avoided when the heavier fractions are desired. The different fractions may be designated and identified as follows:

<i>Name.</i>	<i>Fraction.</i>	<i>Constituents.</i>
	Boiling-point.	
Cymogene,	0° C.	
Rhigolene,	18° C.	
Petroleum ether,	$40 - 70^{\circ}$ C.	$C_5H_{12} + C_6H_{14}$
Petroleum naphtha or ligroin,	$80 - 120^{\circ}$ C.	$C_6H_{14} - C_8H_{18}$
Petroleum benzin or benzoline,	$120 - 150^{\circ}$ C.	$C_8H_{18} - C_9H_{20}$
Kerosene, photogene, head-		
light oil,	$150 - 300^{\circ}$ C.	$C_{10}H_{22} - C_{16}H_{34}$
Lubricating oil (also called paraffin oil)—Sp. gr. 0.87 to 0.94.		
Petrolatum,	Melting-point varies from 45 to 48° C.	
Paraffin wax,	Melting-point varies from 52° to 80° C.	
Coke,		

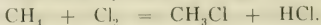
NOMENCLATURE OF THE HYDROCARBONS.

The hydrocarbons of the paraffin series are always denoted by the termination "ane." The first four members of the series, methane, ethane, propane and butane, have special names. The remaining members of the group are usually denoted by the Greek or Latin numeral corresponding to the number of carbon atoms in the molecule. Thus, C_5H_{12} is called pentane; C_8H_{18} is called octane; $C_{12}H_{26}$ is called dodecane; and $C_{31}H_{64}$, hentriacontane, etc. It is, however, necessary to consider other groups of atoms which do not exist in the free state, but which are derived from the above hydro-

carbons by the removal of a hydrogen atom. These, it will be seen, are *not saturated*; they have the *general formula* C_nH_{2n+1} , and are usually denoted as “unsaturated hydrocarbons,” *hydrocarbon radicals* or, more commonly, *alkyl radicals* or groups. Individually, they are denoted by changing the termination of the corresponding hydrocarbon from “ane” to “yl.” In this way, from methane (CH_4) we obtain methyl (CH_3); from ethane (C_2H_6) we obtain ethyl (C_2H_5); from propane (C_3H_8), propyl (C_3H_7); from dodecane ($C_{12}H_{26}$), dodecyl ($C_{12}H_{25}$). The general name *saturated hydrocarbons* (because they are saturated with hydrogen), is frequently interchangeable with *paraffins*, because one of the substances obtained from this series, and which is a mixture of the higher members, is *paraffin wax*. The word paraffin is derived from two Greek words—“*parum*” little, and “*affinis*” affinity—indicative of their resistance to the action of the chemical reagents. Petroleum, for instance, which may be taken as a type of the hydrocarbons, is not affected by either HCl , H_2SO_4 , Br_2 nor I_2 , but freely by Cl_2 .

ADDITION AND SUBSTITUTION.

Chlorin, as is well known, combines directly with the paraffins, and the action is best promoted by sunlight. Thus, we find upon examination of such a reaction, two different compounds resulting, which may be illustrated by the following reaction:

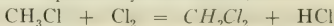


One of the products is monochlormethane, com-

monly called methyl chlorid, the other is hydrochloric acid. If, however, we allow chlorin to act on carbon monoxid (carbonyl), as in the formation of carbonyl chlorid (phosgene), a different reaction takes place. To illustrate, $\text{CO} + \text{Cl}_2 = \text{COCl}_2$. The compound having the formula COCl_2 is the only product of the reaction. In the first reaction we have removed one of the hydrogens of the compound CH_4 , and replaced it with a chlorin atom. In the second reaction we have added all of the chlorin directly to the carbonyl, replacing nothing and forming no by-product. The formation, therefore, of methyl chlorid illustrates *substitution*, while the formation of carbonyl chlorid illustrates *addition*. Among the aromatic products we find many practical illustrations of addition and substitution. To illustrate, starting with benzene, C_6H_6 , we obtain several benzene chlorids, as benzene dichlorid, $\text{C}_6\text{H}_6\text{Cl}_2$; benzene tetrachlorid, $\text{C}_6\text{H}_6\text{Cl}_4$, and benzene hexachlorid, $\text{C}_6\text{H}_6\text{Cl}_6$. These, it will be seen, are addition (additive) products. On the other hand, such derivatives of benzene as monochlorbenzene, $\text{C}_6\text{H}_5\text{Cl}$; dichlorbenzene, $\text{C}_6\text{H}_4\text{Cl}_2$; pentachlorbenzene, C_6HCl_5 , and hexachlorbenzene, C_6Cl_6 , are known as substitution (substitutive) products. It is necessary that the student be able to clearly distinguish between these two classes of derivatives. The nomenclature of these classes, illustrated above, may further be exemplified by the following parallel from inorganic chemistry: benzene dichlorid ($\text{C}_6\text{H}_6\text{Cl}_2$), which is an addition product, may be

compared to carbon disulfid (CS_2); whereas the substitution products may be distinguished by attaching the name and numerical value of the substitutive element or group to the fundamental name. For example, to the compound $\text{C}_6\text{H}_4\text{Cl}_2$, in which it will be seen that *two chlorin* atoms were substituted for *two hydrogen* atoms of the benzene, the name *dichlorobenzene* is given. Another way of distinguishing between these two is by mentioning the fundamental name first and the additive group last in the addition products, and the substitutive group first and the fundamental name last in the case of substitution products.

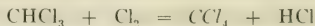
Further illustration may be drawn from the action of chlorin upon marsh gas. We have seen at the beginning of this chapter that when marsh gas has been acted upon by chlorin, methyl chlorid and hydrochloric acid were formed. By further action of chlorin on the so produced chlorids, the entire hydrogen in the molecule of methane may be substituted or replaced by the chlorin; thus:



Dichlormethane, also called methylene chlorid:



Trichlormethane, also called methenyl chlorid or chloroform:



Tetrachlormethane, also called carbon tetrachlorid.

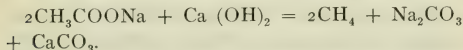
Of these the *tri*- and *tetra*-haloid derivatives are the only ones of practical importance owing to their use in the arts and in medicine.

HOMOLOGUES OF METHANE.

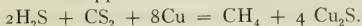
METHANE is the simplest of all carbon compounds in that it contains the lowest number of carbon and hydrogen atoms. Its formula (CH_4) structural

formula, $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$, shows it to contain but one

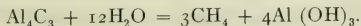
carbon atom. It can be synthesized in the laboratory by heating together sodium acetate and lime:



Another method consists of passing a mixture of hydrogen sulfid and the vapor of carbon disulfid over red-hot copper:



A third method of producing marsh gas is by the action of water on aluminum carbid, according to the following reaction:

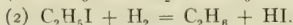
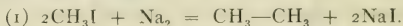


Lastly, it may be separated from coal gas, of which it constitutes 34%.

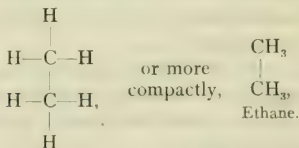
Description.—Methane is a colorless, tasteless gas which may be condensed to a liquid by high pressure at very low temperatures. Chemically, methane is very stable, it kindles at a higher temperature than either hydrogen or amorphous carbon which accounts for the efficiency of the Davy safety lamp. With chlorin, methane forms a violently explosive mixture,

especially in direct sunlight. This action is modified somewhat in diffused daylight.

ETHANE (C_2H_6), the second member of the paraffin series, may be prepared by treating alkyl halid with metallic sodium or zinc (alkyl halids are compounds of a hydrocarbon radical with a halogen), or it may be prepared by warming ethyl iodid with zinc-copper couple and water:



There is also an electrolytic method for the production of ethane. From the method of its preparation we may regard ethane as composed of two methyl groups united together

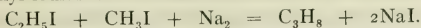


(C_2H_6); or we may regard it as composed of the alkyl ethyl, and hydrogen, C_2H_5-H . = ethyl hydrid.

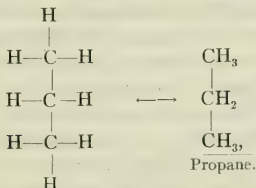
Properties.—Ethane is a gas condensable to a liquid more readily than methane. Liquid ethane has a boiling-point of $-90^\circ C$. Ethane burns with a luminous flame and in every other respect closely resembles methane. Examination of its methods of preparation uniformly show that the ethyl group must contain one methyl group.

PROPANE (C_3H_8). Propane is a gas which can

be prepared by treating a mixture of methyl and ethyl iodids with metallic sodium:



It may also be prepared from zinc propyl or from propyl iodid. Its graphic formula is



Properties.—Propane is a colorless gas which condenses to a liquid at -18°C . Chemically, it seems more readily affected by a few of the reagents than the preceding two hydrocarbons, but seems very indifferent toward most of the reagents. Its formula contains 3 carbon atoms and may be written $\text{CH}_3-\text{CH}_2-\text{CH}_3$, from which it will be seen that it contains at least two methyl groups.

BUTANES (C_4H_{10}). Butane is a gas which can be prepared by treating 2 molecules of ethyl iodid with metallic sodium or zinc. Thus:



Normal butane condenses to a liquid which boils at

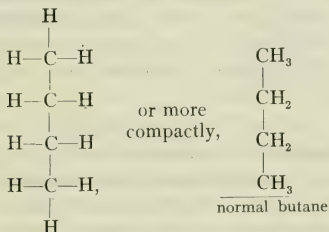
1°C . Iso-butane, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array} - \text{CH}_3$, boils at -17°C .

Curious as it may seem, some substances having the same elements and percentage composition are

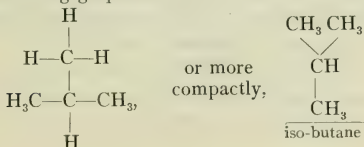
sometimes different in their nature and properties. Thus, in the synthesis of butane, by a slight difference in the method of its preparation, we obtain a compound which has the formula C_4H_{10} , which, as we know is the formula for butane, but whose boiling-point is $-17^\circ C$. Furthermore, substitution products of these two butanes have different properties. In cases of this nature we call this new butane an *isomer of butane*. Frequently two, and often more substances having the same percentage composition are met with. These are all spoken of as isomers of the normal parent body, and owing to this important property we have the numerous organic compounds. The number of possible isomers increases amazingly as the carbon atoms in the molecule increase in numbers. Thus, while we have but one methane and one ethane and propane, we have two butanes, three pentanes, five hexanes, nine heptanes, eighteen octanes, thirty-five nonanes, seventy-five decanes, one hundred and fifty-nine undecanes, three hundred and fifty-four dodecanes, eighteen hundred and two triadecanes. While not all of these isomerids of the hydrocarbons $C_{13}H_{28}$ have been prepared, it is a fact that in the case of pentane, where three possibilities of isomerism exist, all three have actually been prepared. In the case of hexane, where five isomerids are possible, all five have been prepared, and their boiling-points have been determined.

The chemical basis for isomerism is that the difference in properties of the different isomerids is

explained by a difference in the arrangement of the atoms in the molecule. In other words, it is a question of the atomic arrangement in the molecule. Thus, we can determine the structure of *normal* butane by its synthesis from ethyl iodid and sodium, and prove it has a straight chain of carbon atoms. Its graphic formula is



From the above graphic formula we see that the substance may be termed *diethyl*, $\text{C}_2\text{H}_5 - \text{C}_2\text{H}_5$. We may also consider the formula of normal butane to be a derivative of propane by attaching a carbon atom with its saturating hydrogen atoms to one of the end carbon atoms of propane. There is, however, a different arrangement possible in which the four carbon atoms and the ten hydrogens form a branched or a forked chain and not a straight one, according to the following graphic formula:

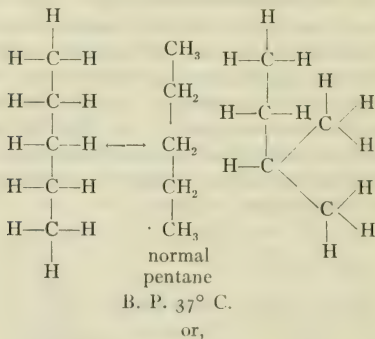


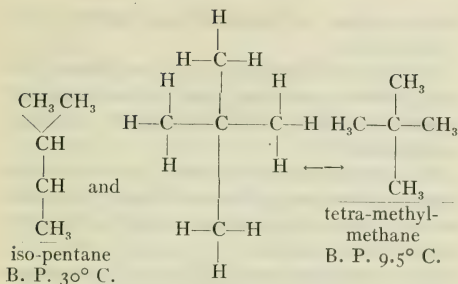
This second arrangement may be said to be derived from propane by attaching a fourth carbon atom to the middle carbon atom of propane. The graphic formula, it will be seen, represents a central carbon atom attached to three methyl groups, so it may be regarded as a methane in which three methyl groups are substituted for three hydrogens. We may safely apply to it the name of trimethylmethane, $\text{CH}(\text{CH}_3)_3$. The above graphic formula agrees with the synthesis of isobutane from tertiary butyl iodid by reduction:



Therefore, *all compounds having a forked or branched chain are known as iso compounds*, and their names are preceded with the word "iso."

The following are three graphic formulas of the isomers of pentane:





The above graphic formulas for pentane illustrate an important fact: that it is possible to construct as many *formulas* as there are *isomerids*. Example: it is only possible to construct three different graphic formulas for a substance having the molecular formula C_5H_{12} , and only three isomers of pentane are known. More could not be represented by graphic formulas, assuming always that carbon is tetravalent. This agreement between theoretic conclusions and observed facts strongly evidences the tetravalent character of carbon.

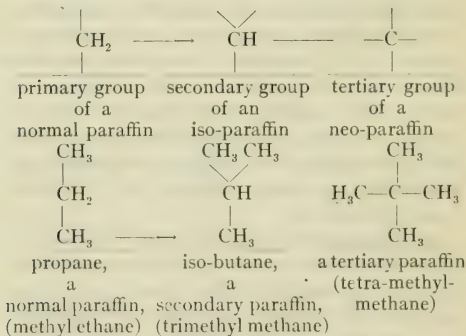
The Nomenclature of the Isomeric Paraffins.—In the case of the different isomers, different distinguishing terms are employed; thus, *normal*, *iso* and *neo-paraffins*. To illustrate: in a *normal*, sometimes called *primary*, paraffin, a straight carbon chain exists in which each middle carbon atom is attached to two other carbon atoms and two hydrogen atoms. It may be said that normal paraffins con-

tain the group $= \text{CH}_2$, which is sometimes called *primary group*.

An *iso*-paraffin contains at least one carbon atom united directly with three other carbon atoms and contains the group $\equiv \text{CH}$, sometimes called the *secondary group*.

A *neo*-paraffin, sometimes called tertiary paraffin, contains at least one carbon atom directly combined with four others, and contains the group $\equiv \text{C}$, also termed a tertiary group.

Below are given graphically the three groups characteristic of the three classes of paraffins, and following these, three examples of paraffins representing each class:

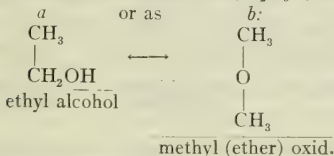


In the case of the “iso” and the “tertiary” hydrocarbons, it is sometimes convenient to use a name which often expresses readily the constitu-

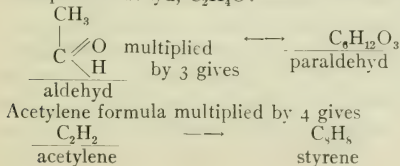
tion of a compound (examine the names given in brackets).

Isomerism is of two kinds: (1) Metamerism.—Substances which have the same percentage composition and the same molecular weight are said to be *metameric*. Thus, the formula C_2H_6O is characteristic of both ethyl alcohol and methyl ether. These substances, therefore, are *metameric*. (2) *Polymerism.*—Substances which have the same percentage composition, but different molecular weights, are said to be *polymeric*. Thus, C_2H_4O is the formula of aldehyd; this formula multiplied by 3 will give us $C_6H_{12}O_3$, which is the formula for paraldehyd. Again, acetylene has the formula C_2H_2 ; benzene, C_6H_6 , and styrene, C_8H_8 . These, therefore, being multiples of acetylene, are polymeric.

(1) Metamerism is shown thus, C_2H_6O , may exist as



(2) Polymerism is shown in paraldehyd, which is a multiple of aldehyd, C_2H_4O :



FORMULAS.

While symbols are used to express atoms, formulas are used to express molecules. Formulas are of three kinds: (1) the *empiric* formula, which represents the elements present in a compound and the relative proportion of each. Thus, the formula C_2H_6O may indicate either a compound having the formula $C_4H_{12}O_2$ or one having the formula $C_8H_{24}O_4$, etc. If, by the determination of its vapor density, we find it to be $C_4H_{12}O_2$, in such a case the formula showing the number of atoms in the molecule and their relative numbers is called *molecular* formula. (2) *Rational* formula, also called *constitutional* formula indicates the probable arrangement exhibited in the formula; also by a characteristic group present, the class the compound belongs to. (3) *Graphic* formula, also called *structural* formula, represents the arrangement of the atoms in a molecule and the probable relations of one to another. Examples:

<i>Empiric formula.</i>	<i>Rational formula.</i> (constitutional.)	<i>Graphic formula.</i> (structural.)
C_2H_6O	C_2H_5OH	$ \begin{array}{c} H \\ \\ H-C-H \\ \\ H-C-OH \\ \\ H \end{array} $
alcohol	alcohol	alcohol

CHAPTER XXII.

ETHYLENE SERIES.

THE second of the series of hydrocarbons is the ethylene series, so called from the first member of the series. This series is sometimes called the "ethene series" or the "olefins." The general formula of the series is C_nH_{2n} . Whereas, in the paraffin series we cannot form the halogen derivatives without substituting one or more hydrogen atoms of the paraffins, in the ethylene series we can form addition products directly without substituting the hydrogen atoms in the molecule. Therefore, we call the methane series *saturated* because they cannot unite directly with elements or compounds; whereas the ethylene series of hydrocarbons, because they do combine directly with other elements or compounds, we call *unsaturated*. This unsaturation depends on the difference in the relation between the carbon atoms. Thus, in the case of ethane, we find it to be composed of two methyl groups which, when united, again form a saturated hydrocarbon with no free bonds. The two methyls are united by one bond. This bond which, in a former chapter we called the paraffinic bond, is very strong and tenaciously resists any attempt to break it up. In the case of the olefins, we find the carbons united by a double bond which we have previously called the olefinic bond. Now, one would suppose that the carbon atoms,

being united by two bonds would form much stronger union in the case of the olefins than they would in the case of the paraffins, where but single bond union exists. Such, however, is not the case. The paraffinic bond is much stronger than the olefinic.

The relation of the carbon atoms in the ethylene series is usually represented in the graphic formulas by two bonds. The following are the first six members of the ethylene series with their empiric and graphic formulas:

TABLE OF THE OLEFINS.

(C_nH_{2n} .)

<i>Name.</i>	<i>Mol. Form.</i>	<i>Mol. Wt.</i>	<i>B. Pt.</i>	<i>Graph. Form.</i>
Ethylene,	C_2H_4	28	$-103^\circ C.$	$\begin{array}{c} CH_2 \\ \\ CH_2 \end{array}$
Propylene,	C_3H_6	42	$-48.5^\circ C.$	$\begin{array}{c} CH_2 \\ \\ CH \\ \\ CH_3 \end{array}$
Butylene,	C_4H_8	56	$-5^\circ C.$	$\begin{array}{c} CH_2 \\ \\ CH \\ \\ CH_2 \\ \\ CH_3 \end{array}$
Amylene,	C_5H_{10}	70	$40^\circ C.$	$\begin{array}{c} CH_2 \\ \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_3 \end{array}$

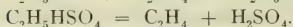
<i>Name.</i>	<i>Mol. Form.</i>	<i>Mol. Wt.</i>	<i>B. Pt.</i>	<i>Graph. Form.</i>
Hexylene,	C_6H_{12}	84	68.° C.	$ \begin{array}{c} CH_2 \\ \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_3 \end{array} $

Chemical Properties of the Olefins.—The olefins unite directly with other substances, particularly the halogens and the hydracids. The members of the series are homologous and differ from one another by the group CH_2 . They are also polymeric; they bear a simple ratio to the paraffins, each member containing two hydrogen atoms less than the paraffin having a corresponding number of carbon atoms. They likewise bear a simple relation to each other in point of their molecular weights. Thus, the members differ from one another in their molecular weights by 14. The chemical properties of ethylene apply to the whole group. Thus, with bromine they form bromethylenes, with hydrogen they form the corresponding paraffins, and with halid acids they form the monohalogen derivatives of the paraffins.

Ethylene, C_2H_4 , also called olefin, olefant gas (so called from *oleum*, oil, and *fians*, forming; because with the halogens it forms oily liquids) and ethene; it is the first member of the series of that name. One would suppose that, in order to correspond to the paraffins, *methylene*, CH_2 , ought to be the first member of this series, but all attempts to

synthetize or isolate such a compound have been unsuccessful. Yet a number of important compounds, such as carbon monoxid and hydrocyanic acid, are sometimes considered as the derivatives of methylene.

Preparation.—(1) Ethylene is best prepared by mixing ethyl alcohol with strong sulfuric acid and heating the mixture to 175°C . Two reactions occur, the first one forming ethyl sulfuric acid, with the elimination of water; the second one forming ethylene, with the elimination of sulfuric acid, according to the following equations:



(2) It may be prepared by decomposition of the monohalid derivatives of ethane by alcoholic solution of an alkalin hydroxid. This is a very important reaction for the preparation of the homologues of the ethylene series. Thus, any paraffin alkyl halid, by treating it with alcoholic solution of potassium hydroxid, will decompose into hydrobromic acid and form the corresponding homologue of ethylene. Reaction:



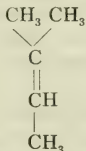
Properties.—Ethylene is a colorless gas having a peculiar, disagreeable odor, burns with a luminous, smoky flame; with air and oxygen it forms explosive mixtures; it is irrespirable and is an important constituent of illuminating gas, the luminosity of which depends greatly upon the amount of ethylene it contains. It unites directly with chlorin, volume for volume, forming an oily liquid having the com-

position $C_2H_4Cl_2$, ethylene dichlorid, commonly known as "Dutch liquid," owing to its having been discovered by four Dutch chemists.

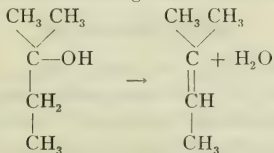
Besides ethylene chlorid, the other *halid derivatives* are: ethylene bromid, $C_2H_4Br_2$, and ethylene iodid, $C_2H_4I_2$.

Physical Properties.—In point of aggregation, the olefin series is very similar to the paraffins. Thus, the *first four* members are *gases*, the next *thirteen* are *liquids* and the remainder are colorless solids. The first two members have no isomers, but there are three isomeric butylenes, four isomeric amylenes six heptylenes, six octylenes and two nonylenes, all of which have been prepared.

Of the amylenes, *isoamylenes*, trimethylethylene, commonly known as *pental*, has the formula

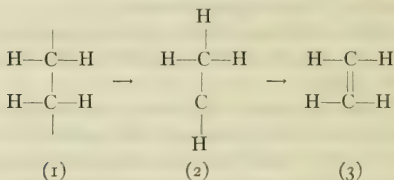


It is prepared, like the other olefins, by dehydrating isopentyl alcohol according to the following formula:



Pental has been used successfully as an anesthetic.

Structure of Ethylene.—Three theoretic formulas have been assigned for ethylene:



Of these the first formula, representing carbon atoms as practically trivalent and showing the two free bonds, would seem to be the most probable. If this were the true structure of ethylene, the independent existence of the alkyls, methyl, ethyl or propyl, etc., would also seem possible. This, however, is not the case. The same difficulty seems to hold with the second formula. The third formula, therefore, most probably expresses the true structure of ethylene.

Nomenclature.—The names of the olefins correspond to the names of the paraffins, with the exception that the vowel "a" of the first series has been replaced by the vowel "e."

ACETYLENE SERIES.

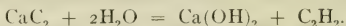
Acetylene, C_2H_2 , also called ethine, is the first member of the third series of hydrocarbons, and after it the series has been named. In this series the carbon atoms are linked by three bonds. The general formula of the series is $\text{C}_n\text{H}_{2n-2}$. They are

unsaturated and unite *directly* with four atoms of the halogens or with two molecules of the haloid acids without any loss of hydrogen, and through such addition are converted into substitution products of the paraffins. Their structural formula shows them to contain at least one CH group. This group, when it is adjacent to the acetylenic bond (triple bond), always precipitates ammoniacal solutions of silver nitrate, which no other hydrocarbon will do.

THE ACETYLENES.

(C _n H _{2n-2} .)			
<i>Name.</i>	<i>Mol. Form.</i>	<i>B. Pt.</i>	<i>Graphic Formula.</i>
Acetylene (or ethine),	C ₂ H ₂	-84° C.	$\begin{array}{c} \text{C}-\text{H} \\ \\ \text{C}-\text{H}. \end{array}$
Allylene (methyl acetylene, propine),	C ₃ H ₄	gas	$\begin{array}{c} \text{C}-\text{H} \\ \\ \text{C} \\ \\ \text{C}\equiv\text{H}_3. \end{array}$
Crotonylene (ethyl acetylene, and butine),	C ₄ H ₆	18° C.	$\begin{array}{c} \text{C}-\text{H} \\ \\ \text{C} \\ \\ \text{C}=\text{H}_2 \\ \\ \text{C}\equiv\text{H}_3. \end{array}$
Valerylene (propyl acetylene or pentine),	C ₅ H ₈	45 to 50° C.	$\begin{array}{c} \text{CH} \\ \\ \text{C} \\ \\ \text{C}=\text{H}_2 \\ \\ \text{C}=\text{H}_2 \\ \\ \text{C}\equiv\text{H}_3. \end{array}$

Preparation and Properties.—(1) By the action of calcium carbide on water:



(2) By the direct union of the elements, such as occurs on passing electric sparks between carbon electrodes in the presence of hydrogen:



(3) By passing chloroform vapor over red-hot copper:



The first method is important commercially because it is employed in the manufacture of acetylene gas for illuminating purposes. The structural formula of acetylene shows the carbon atoms to be linked by three bonds. The significance of this "acetylenic" bond is not clear at the present time. This bond is very unstable as the nature of acetylene proves. The gas cannot be stored under pressure, and in the liquefied form it is not valued commercially. When heated sufficiently, high acetylene forms the polymeric benzene, C_6H_6 , and styrene, C_8H_8 . It unites directly with the halogens, especially bromine and hydrobromic acid, forming tetrabromethane and ethyl bromide.

Nomenclature.—Compounds having the triple union have names ending in "ine." Thus the third member is officially called "propine." In the present work, however, we have adhered to the older and better understood nomenclature. This series contributes two acids of pharmaceutical interest, namely crotonic acid, $\text{C}_4\text{H}_6\text{O}_2$, and oleic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$.

COAL GAS.

Coal gas is produced by subjecting coal to "*dry*" or "*destructive*" *distillation*.

Destructive distillation consists in heating a non-volatile organic matter (coal or wood) in such a manner that air is excluded and the organic body is decomposed, giving rise to new compounds—*products of decomposition*.

Coal gas, therefore, is a mixture of gases (products of the decomposition of coal), consisting mainly of hydrogen and the hydrocarbons. Coal is heated in iron retorts without contact of air, and the products of decomposition are cooled in condensers, where the heavy coal-tar and the lighter gas-liquor properly cooled are collected in tanks. The gas which remains uncondensed is passed through tanks filled with wetted coke for the purpose of dissolving the ammonia. Next the gas is led through chambers containing either ferric hydroxid or slaked lime, spread upon shelves for the purpose of ridding the gas of sulfurated gases, such as carbon disulfid, hydrogen sulfid, ammonium sulfid, etc. When slaked lime is employed as a purifying agent it absorbs carbon dioxid as well. The gas so purified is finally stored in large gas tanks.

COMPOSITION OF COAL GAS.

Hydrogen,	}	52%	by volume.	These three gases serve as <i>diluents</i> of the heavy hydrocarbon <i>illuminants</i> and preclude smoky flames.
Methane,		34%		
Carbonic oxid,		6%		

Ethylene	}	4% by volume	These three gases are the <i>illuminants</i> in coal gas.
Acetylene			
Benzene			
Ammonia gas	}	4% " "	These four gases are the usual <i>impurities</i> of gas.
Nitrogen			
Carbon disulfid			
Carbon dioxid			

It will be seen from the above analysis that the "dilutents" constitute about 90% of coal gas, while the "luminants," rich in carbon and to which the luminosity of the flame is due, constitute but 4% by volume of the gas. The impurities are due to nitrogen (a product of decomposed air which enters the retorts in the process of charging them), ammonia, carbon dioxid and the sulfids which escape the purifiers.

STRUCTURE OF GAS FLAME.

A gas flame may be said to consist of three layers: the innermost layer consisting of unburnt gases; the middle layer or luminous layer, consisting of partially burnt gases and minute particles of carbon, which latter impart to the flame its reducing properties and the name "reducing flame" (R. F.); the outermost layer which is colorless, consisting of completely burnt gases. This layer in which the carbon and hydrogen are completely oxidized is the hottest of the three and is called the "oxidizing flame" (O. F.).

The innermost flame, therefore, is a mixture of gas and air, the middle layer to which the oxygen of the air, owing to the great heat of the oxidizing

flame, has no access, consists of partly burnt hydrocarbons with particles of carbon rendered incandescent so as to emit white light.* Free carbon can be detected in this layer by introducing a piece of white porcelain into the flame when the carbon will deposit on it as soot.

In the outermost layer the hydrocarbons are "oxidized" or "burnt" to carbon dioxide and water. This, therefore, is the "hottest" flame.

If air is mixed with gas before its ignition, as in the case of the "Bunsen burner," both the carbon and hydrogen become completely "burnt up," furnishing a colorless or "Bunsen flame." A Bunsen burner consists of a gas-jet, the base of which is provided with a perforated *collar* which admits the air into the jet.

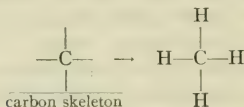
The temperature of gas flame is very high, that of a flat burner about 1300° C., and that of a Bunsen burner about 1500° C.

The "Welsbach incandescent burner" has effected an enormous economy in gas consumption. Thus, the 86% of hydrogen and methane present in gas, and which in the ordinary burner produce barely any light, is utilized in rendering the infusible mantle of the incandescent burner hot, and thus produce a strong white light.

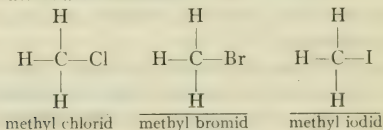
CHAPTER XXIII.

DERIVATIVES OF METHANE.

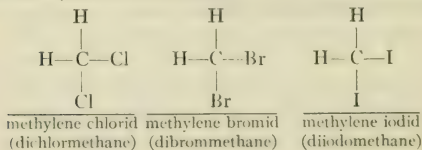
THE structural formula of methane, CH_4 , is the following:



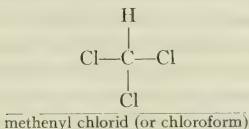
If *one* of the hydrogen atoms is substituted by an atom of any other *univalent element* or a *univalent group* of elements, a “*mono-substitution*” derivative is produced. Thus, by substituting the hydrogen atoms of methane with the halogens the following derivatives are obtained:



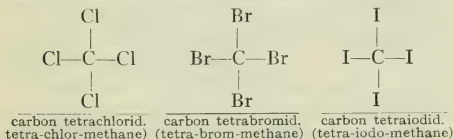
If *two* hydrogens of methane are replaced by *two univalent* or *one divalent atom or group*, a “disubstitution” product is obtained; thus:



If *three* hydrogen atoms in methane are substituted by *three monads*, or *one dyad and one monad*, or by a *triad* atom or group, a “trisubstitution” product is obtained:



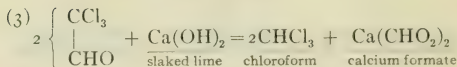
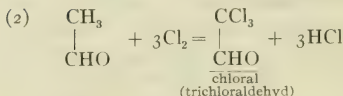
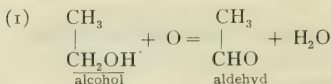
If *all* of the hydrogen of methane is substituted by other atoms or groups of atoms, “tetra-substitution” products are obtained:



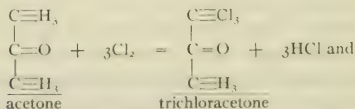
Of the above halogen derivatives *only* the *tri-* and *tetrasubstitution* products are of *practical* importance to pharmacy and the arts.

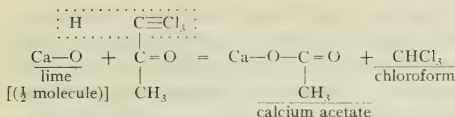
CHLOROFORM.—Trichlormethane (chloroformum U. S. P.)— CHCl_3 (Souberain and Liebig, 1831) is prepared by heating a mixture of chlorinated lime (calx chlorinata), alcohol and water. The mixture when distilled yields chloroform which passes over with the water-vapor and is condensed together with the water, from which it separates owing to its higher specific gravity. It is then redistilled from calcium

chlorid which absorbs the water. The reaction is very complex, and it is supposed that three changes occur in its formation. The first change depends upon the oxygen in the bleaching powder which converts the alcohol into *aldehyd*; the second change depends upon the action of chlorin on the alcohol and the formation of *chloral*; the third, upon the decomposition of the chloral by the alkalin lime (of the bleaching powder) into chloroform and calcium formate. To illustrate:



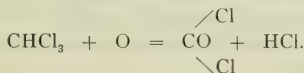
Lately the production of chloroform from acetone has almost entirely superseded the process just given. This latter process depends upon the formation of trichloroacetone which, upon being heated with lime, is converted into chloroform and calcium acetate; thus:





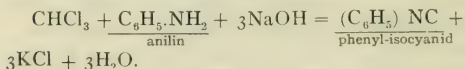
Description, Uses and Tests.—Chloroform is a colorless, heavy-thin (limpid) liquid, having a sweetish taste and a characteristic (chloroformic) odor. The specific gravity of pure chloroform is 1.525. The official variety, containing a little alcohol for the purpose of preservation, has a specific gravity of 1.497 and a boiling-point of 61° C. It is readily soluble in alcohol (constituting the official spirit), ether, etc., and to the extent of 0.5% in water (1:200), forming the official chloroform water (aqua chloroformi U. S. P.). It ignites with difficulty and burns with a greenish, smoky flame.

Chloroform is *used* as a solvent for fats, resins, caoutchouc, phosphorus, sulfur and iodine. The commercial variety contains aldehyde, alcohol, etc., from which it can be purified by mixing it with sulfuric acid, separating from this acid, neutralizing with a solution of sodium carbonate, separating from this solution, adding lime to dehydrate it and finally distilling it on a water-bath, adding to the distillate from one-half to one per cent. of alcohol to prevent the formation of its impurity, carbonyl chlorid (COCl_2), so-called phosgene gas.

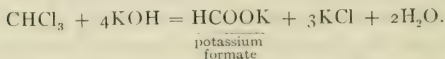


Tests for Purity.—Pure chloroform should not color solution of sulfuric acid and chromic oxid green, nor should it discolor solutions of KOH, KI or H₂SO₄. It should not precipitate silver nitrate. In medicine chloroform is extensively used as an anesthetic (Simpson, 1848). For this purpose it should never be administered in a room illuminated with gas, because the traces of CO which escape combustion, at once combine with the chloroform forming the strongly irritating and irrespirable phosgene gas. As an anesthetic it is safer for children and women in parturition than for other adults. Externally it is an irritant or vesicant.

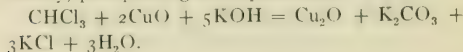
Tests.—(1) Chloroform in solutions may be detected by warming together some of it with alcohol, solution of sodium hydroxid and a few drops of anilin, when a strong, irritating and poisonous vapor of *phenyl-isocyanid* is produced:



(2) Heated with an alcoholic solution of potassium hydroxid (saponified), it gives potassium formate and chlorid:

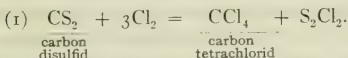


(3) Chloroform reduces "Fehling's solution" readily, precipitating red cuprous oxid:

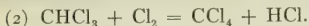


(4) When chloroform is mixed with a solution of betanaphthol in strong potassium hydroxid and the liquid heated to about 50°C ., a dark blue color is produced, which gradually changes to green and finally to brown.

CARBON TETRACHLORID.—Tetrachlormethane, CCl_4 , is produced by the action of chlorin on carbon disulfid or on chloroform (Regnault, 1840).



The two products of the reaction are separated by distillation.



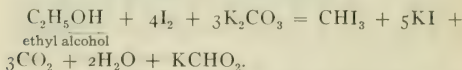
Properties, Uses and Tests.—Carbon tetrachlorid is a heavy, colorless liquid which boils at 77°C . Heated with water to 250°C ., it decomposes into carbon monoxid and hydrochloric acid. Its specific gravity is 1.593 (20°), and it should be noted that the polychlor derivatives have a high specific gravity, and that the corresponding brom- and iodo-derivatives are even heavier than the chlor-products. Carbon tetrachlorid (carbona) is non inflammable and can be used as a fire extinguisher. Like petroleum-benzin, the odor of which it simulates, it is used in extracting fats from refuse materials, in cleansing stained or soiled fabrics and as a solvent in organic chlorinations, it being unaffected by chlorin.

BROMOFORM.—Tribrommethane (bromoformum U. S. P.), CHBr_3 (Lowig, 1832). The commercial bromoform consists of 99% of tribrommethane and

1% of alcohol. It is prepared by methods analogous to the production of chloroform, or by direct bromination of ethyl alcohol dissolved in an aqueous solution of potassium hydroxid, until the latter begins to acquire the color of bromin. It is purified in a similar manner to chloroform, which it resembles in odor and appearance.

Properties and Uses.—Bromoform is a colorless liquid, having a specific gravity of 2.9 (17°) and boiling at 151° C. It is freely soluble in alcohol and ether, but sparingly so in water. It is used in medicine as an anesthetic, antispasmodic and sedative; exhibited in a hydroalcoholic solution or emulsion.

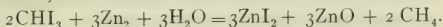
IODOFORM. — Triiodomethane (iodoformum U. S. P.), CHI_3 (Serullas, 1822). It is prepared by precipitating a solution of iodine in potassium iodid with alcohol or acetone in the presence of an alkali carbonate or hydroxid. The yellow powder thus produced can be purified by crystallization from alcohol (hexagonal crystals), or by sublimation (golden yellow leaflets). Reaction:



Properties, Uses and Tests.—Iodoform melts at 119° C., is slightly soluble in water, readily in alcohol, ether, chloroform, benzin, carbon disulfid, fixed and volatile oils. It has a strong antiseptic and anesthetic action (depending on the 96.6% of iodine it contains), and is used as a dressing in surgery. It

possesses a strong, aromatic, saffron-like odor, which can be masked by traces of cumarin, vanillin, naphthalin or oil of bergamot. *Its chief adulterant is picric acid* which may be detected by agitating the sample with a solution of KOH, carefully neutralizing with acetic acid; upon adding KNO_3 , a yellow precipitate of potassium picrate is deposited. A water solution of iodoform should not yield a precipitate with BaCl_2 (sulfates) or with AgNO_3 (chlorids).

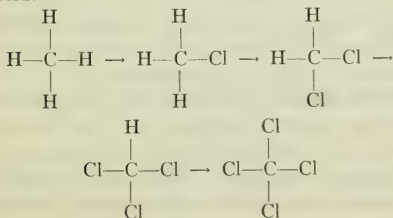
Iodoform is hydrolyzed by alcoholic potash in a similar manner to chloroform. When heated with zinc dust and water, iodine is evolved and methane formed; thus:



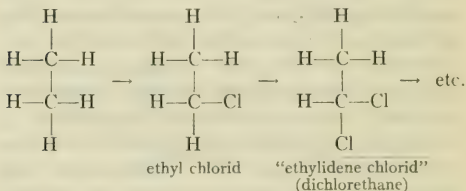
CARBON TETRAIODID.— CI_4 , was at one time introduced as "odorless iodoform." It is prepared in a manner similar to carbon tetrachlorid. •

DERIVATIVES OF ETHANE.

Under Methane we have seen that by a process of gradual substitution of chlorine for the hydrogen of marsh gas, we have changed it into carbon tetrachlorid:



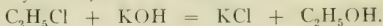
In a like manner, bromin, iodin and other mono-, di-, tri-, and tetra-substitution products may be formed from methane as well as other hydrocarbons. Thus, from ethane we may get the following:



The halogen derivatives of ethane are less important and interesting than those of methane.

ETHYL CHLORID, $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{Cl} \end{array}$, is a limpid, colorless

liquid, boiling at 12.5°C . It burns with a greenish, smoky flame, is but sparingly soluble in water, but freely in alcohol (this solution is called "chloric ether") and ether, etc. When heated with potassium hydroxid, it forms alcohol:



When it is treated with chlorin in direct sunlight, it yields the di-, tri-, tetra-, etc., substitution products of ethane. Used as local anesthetic.

ETHYL IODID, iodoethane, $\text{C}_2\text{H}_5\text{I}$, is formed when a mixture of strong hydriodic acid and alcohol is heated; or by adding to a mixture of red phosphorus and alcohol, iodin, little by little, and then distilling on a water-bath. Ethyl iodid is a highly refractive,

very heavy liquid, having an ethereal odor, boiling at 72° , with a specific gravity of 1.94 (14°), and similar in its properties to ethyl chlorid and iodid.

ETHYL BROMID, $\begin{array}{c} \text{CH} \\ | \\ \text{CH}_2\text{Br} \end{array}$, or bromethane, is

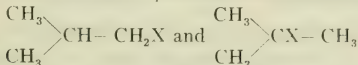
formed when ethane is heated with strong hydrobromic acid, or it can be produced by distilling a mixture of sulfuric acid, alcohol and potassium bromid. The distillate is washed with alkaline carbonate and redistilled from calcium chlorid.

It is a colorless, limpid liquid, with a chloroformic odor and a burning taste, boiling at 38° , and resembles chlorethane in its behavior with alcoholic potash.

Other Monohalogen Derivatives.—The more important are propyl bromid, $\text{C}_3\text{H}_7\text{Br}$; butyl iodid, $\text{C}_4\text{H}_9\text{I}$; propyl iodid has two isomers—*normal* propyl iodid, $\text{CH}_3-\text{CHI}-\text{CH}_3$, boiling at 102° , and *iso*-propyl iodid, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array} \text{CHI}$, boiling at 89.5° . Theoretically, there are four monohalogen derivatives of butane, of which two are produced from normal butane:

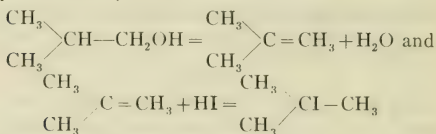
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{X}$ and $\text{CH}_3-\text{CH}_2-\text{CHX}-\text{CH}_3$,

while the other two are produced from isobutane:

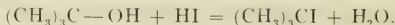


Tertiary butyl iodid, $(\text{CH}_3)_3\text{CI}$, is prepared by treating isobutyl alcohol with sulfuric acid and dis-

solving the so-produced isobutylene in concentrated hydriodic acid; thus:



Another method is by heating trimethylcarbinol with HI; thus:



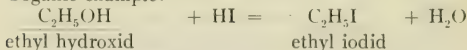
SUMMARY OF THE HALOGEN DERIVATIVES OF THE HYDROCARBONS.

The inorganic compounds of a metal with a hydroxyl group are called *bases* and resemble each other closely, owing to their common constituent—the OH group. Alcohols, on the other hand, are organic compounds, although, like the inorganic bases, they possess the OH group and, like the latter, combine with acids to form water.

Inorganic example:



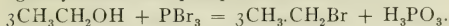
Organic example:



The products so formed are comparable with the salts of inorganic chemistry and are commonly known as “compound ethers” or *esters*. As bases can lose water, forming anhydrids or oxids, so also

can the alcohols. Thus, by abstracting one molecule of water from two molecules of an alcohol, "ethers" are formed. If two alcohols are employed, "mixed ethers" are formed. If an alcohol is treated with a halogen acid, alkyl halids are formed which have been called "halid ethers." Thus, ethyl chlorid, CH_3Cl ; ethyl bromid, $\text{C}_2\text{H}_5\text{Br}$; propyl iodid, $\text{C}_3\text{H}_7\text{I}$, have been termed *halid ethers*.

Preparation.—All the alkyl halids may be prepared by a similar reaction (Gay-Lussac, 1835); that is, by acting with a phosphorous halid on a corresponding alcohol, which yields the corresponding alkyl halid and phosphorous acid; thus:



Properties.—Like the inorganic halids, some of the alkyl halids *slowly* precipitate silver nitrate solution; some, however, do not react with it at all. The alkyl halids can be converted into one another. For example, if ethyl chlorid is heated with potassium iodid, ethyl iodid can be produced.

CHAPTER XXIV.

THE HYDROXIDS OF THE HYDROCARBON RADICALS, OR ALCOHOLS.

AMONG the several classes of the oxygen derivatives of the hydrocarbons are the alcohols, ethers, aldehyds and the acids. These may be said to be the most important classes and all the others to be derivatives of these.

Alcohols are formed when one or more hydrogen atoms of a hydrocarbon is replaced by the corresponding number of hydroxyl (—OH) groups. Alcohols are classified in two ways: (a) According to the number of hydroxyl groups they contain; thus, alcohols containing one hydroxyl group are called *monatomic* or *monacid*; those containing two hydroxyl groups are called *diatomic* or *diacid*; those containing three hydroxyl groups are called *triatomic* or *triacid*, etc. Usually, alcohols containing more than two hydroxyl groups are termed *polyatomic* or *polybasic* alcohols. (b) According to their structure; thus, when the hydroxyl is linked to a carbon atom which is combined with only one other carbon atom, the alcohol is known as a *primary* alcohol, and contains the *univalent primary alcohol group* $\text{—CH}_2\text{OH}$.

Primary alcohols when oxidized yield aldehyd and an acid. When the hydroxyl is linked to a carbon atom which is united with two other carbon

TABLE OF ALCOHOLS.

SHOWING THE RELATIONSHIP BETWEEN THE HYDROCARBON AND THE CORRESPONDING
HYDROCARBON RADICAL AND ALCOHOL.

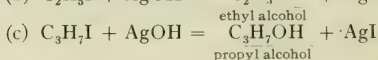
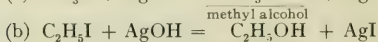
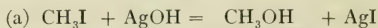
HYDROCARBONS. (C_nH_{2n+2})	ALKYLS. (C_nH_{2n+1})	ALCOHOLS. ($C_nH_{2n+1}OH$)
CH ₄		
C ₂ H ₆	Methane	Methyl Alcohol
C ₃ H ₈	Ethane	Ethyl "
C ₄ H ₁₀	Propane	Propyl "
C ₅ H ₁₂	Butane	Butyl "
C ₆ H ₁₄	Pentane	Pentyl (Amyl) Alcohol
C ₇ H ₁₆	Hexane	Hexyl Alcohol
C ₈ H ₁₈	Heptane	Heptyl "
C ₁₀ H ₂₂	Octane	Octyl "
C ₁₂ H ₂₆	Decane	Decyl "
C ₁₆ H ₃₄	Hexadecane	Cetyl "
C ₂₆ H ₅₄	Hexacosane	Ceryl "
C ₃₀ H ₆₂	Tricontane	Myricyl "
	CH ₃	CH ₃ OH
	C ₂ H ₅	C ₂ H ₅ OH
	C ₃ H ₇	C ₃ H ₇ OH
	C ₄ H ₉	C ₄ H ₉ OH
	C ₅ H ₁₁	C ₅ H ₁₁ OH
	C ₆ H ₁₃	C ₆ H ₁₃ OH
	C ₇ H ₁₅	C ₇ H ₁₅ OH
	C ₈ H ₁₇	C ₈ H ₁₇ OH
	C ₁₆ H ₃₃	C ₁₆ H ₃₃ OH
	C ₂₆ H ₅₃	C ₂₆ H ₅₃ OH
	C ₃₀ H ₆₁	C ₃₀ H ₆₁ OH
	Methyl	
	Ethyl	
	Propyl	
	Butyl	
	Pentyl (Amyl)	
	Hexyl	
	Heptyl	
	Octyl	
	Cetyl	
	Ceryl	
	Myricyl	

atoms, the alcohol is known as a *secondary* alcohol, and contains the divalent secondary alcohol group =CHOH.

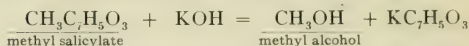
Secondary alcohols when oxidized yield ketones and acids. When the hydroxyl is linked to a carbon atom united with three other carbon atoms, the alcohol is known as a *tertiary* alcohol containing the trivalent tertiary alcohol group $\equiv\text{COH}$.

Tertiary alcohols when oxidized yield compounds containing fewer carbon atoms.

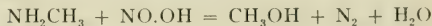
Preparation of the Alcohols.—Alcohols may be formed in several ways: (1) By the action of moist silver oxid upon the alkyl halids; thus:



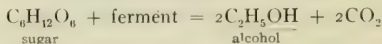
(2) By the saponification of the esters. The decomposition of esters by boiling with alkali hydroxids is usually spoken of as "saponification" with reference to its similarity to the decomposition of fats; thus:



(3) By treating primary amins with nitrous acid; thus:



(4) By the fermentation of fruit juices containing sugars or other carbohydrates:



The production of alcohol by the fourth method will be fully discussed under Ethyl Alcohol.

General Properties of Alcohols.—The alcohols are colorless, neutral substances, among which those containing but few carbon atoms are liquids, while the higher members are solids. The lower members have also a distinctive odor, a burning taste and are soluble in water. These three characteristics—taste, smell and solubility—diminish with the increase in molecular weight. Thus, the first three members are readily miscible with water—butyl alcohol dissolves in 13 parts, amyl alcohol in 40 parts, and so on. The proportion of oxygen present seems to influence its solubility. Thus, cetyl alcohol, $C_{16}H_{33}OH$, which can be prepared from spermaceti, is a water-insoluble solid, very similar to paraffin wax.

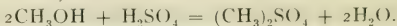
Chemical Properties.—The structure of alcohols is shown by several reactions:

(1) When alcohols are treated with alkali metals, hydrogen is liberated and a compound of the hydrocarbon and the metal is formed. Thus, if methyl alcohol is treated with metallic sodium, the metal is dissolved, and upon evaporation a white, hygroscopic solid is obtained, known as sodium methylate (methoxid), CH_3ONa . When ethyl alcohol is treated in the same manner, a similar compound is obtained, known as sodium ethylate (ethoxid) or, more commonly, sodium alcoholate, C_2H_5ONa . In view of the fact that, immaterial to the quantity of the metal employed, only one atom of hydrogen is

replaced by it, it indicates strongly that only the hydrogen of the hydroxyl group is replaced by the sodium, and thus proves the structure of the alcohols:

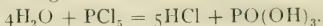


(2) Alcohols combine with acids, neutralizing them and forming water, in which reaction they are distinctly suggestive of the behavior of the metallic hydroxids; thus:



(3) When treated with phosphorus pentachlorid alcohols form alkyl chlorids, hydrochloric and phosphoric acids. An examination of the following reaction will show that one chlorine atom replaces the hydroxyl group in the alcohol, which is very similar to the action of the same reagent upon water; thus:

$4\text{CH}_3\text{OH} + \text{PCl}_5 = 4\text{CH}_3\text{Cl} + \text{HCl} + \text{PO}(\text{OH})_3$,
corresponding to



A characteristic property of all the alcohols is their tendency to form neutral compounds with the acids. These neutral, salt-like bodies are called "ethers" or "esters"; and when oxidized, the alcohols form acids containing two hydrogen atoms less and one oxygen more than the corresponding alcohol.

METHYL ALCOHOL, carbinol, wood alcohol, wood naphtha, wood spirit, methyl hydroxid, CH_3OH .

Properties.—Pure methyl alcohol is a colorless liquid, with odor and taste similar to ethyl alcohol. It boils at 66.7° and has a specific gravity of 0.8. It closely resembles ordinary alcohol in all of its

properties and is used in its stead as a solvent for fats, oils, resins, etc. It burns with a nonluminous flame; taken internally, it intoxicates, and in concentrated form it is highly poisonous. The crude wood alcohol has a disagreeable odor, reminding one of acetone. The purified varieties are marketed under such fanciful names as "Eagle Spirits," "Colonial Spirits," "Columbian Spirits," etc. In Great Britain a tax-free, methylated spirit is employed in the arts; it is a mixture of 10 parts of crude methyl alcohol with 90 parts of common alcohol.

Preparation.—Methyl alcohol (from *meth*, wine, and *ule*, wood) is obtained by the destructive distillation of wood. (Boyle, 1661.)

When wood is subjected to destructive distillation without access of air, it yields inflammable gases, an aqueous, strongly acid distillate, some tar, and the residue is wood charcoal. The operation is carried out in large iron retorts, and the products may be summarized as follows:

Gases, 25%.	{	Carbon monoxid, dioxid, methane, acetylene, ethylene and propylene.
Noncondensable.		
Vapors 50%.	{	Acetone, furfurol, methyl alcohol, methylamin and acetic, formic, butyric, crotonic, capronic and propionic acids.
Condensable acid liquid.		
Tarry liquid, 10%.	{	Creasote, toluol, xylol, cumol, methol, creasol, phlorol, naphthalin, pyrene, chrysene and paraffin.
Residue, 15%.		
		Charcoal and inorganic salts.

The aqueous distillate contains methyl alcohol mixed with acetic acid, acetone and methyl acetate. This mixture is known as *pyroligneous acid* and sepa-

rates from the tarry liquid on standing, when it is decanted. It is next neutralized with lime, whereby the acetic acid is converted into lime acetate. This mixture is then subjected to distillation. The volatile methyl alcohol and acetone, together with water, pass into the receiver and form the *crude wood spirit*. This is further purified by fractional distillation over quicklime, which separates the greater part of the acetone which has a lower boiling-point (56°). Lately, wood alcohol has also been produced by subjecting the by-products of the beet-sugar industry to destructive distillation. The molasses is fermented and the ethyl alcohol is removed by distillation. The solid residue is then dried and distilled like wood (see description in previous paragraph).

ETHYL ALCOHOL, ethyl hydroxid, "grain alcohol" or common alcohol (alcohol U. S. P.), C_2H_5OH . Ethyl alcohol is obtained by the fermentation of certain carbohydrates, most particularly glucose with yeast (vinous fermentation, also called alcoholic fermentation). It has been shown that fermentation may be caused by the presence of small organisms, either of vegetable or animal origin, known as ferments. There are several kinds of ferments. The one causing alcoholic fermentation is zymase, a vegetable ferment contained in ordinary yeast. These ferments are sometimes called enzymes and are divided into organized and nonorganized ferments. These include pepsase (pepsin), the enzyme of gastric juice; trypase (trypsin), the enzyme of the pancreatic

juice; diastase, found in malt; amylopsase (amylopsin), found in pancreatic secretion and similar to diastase; invertase, found in yeast, hydrolyzes sucrose to a mixture of dextrose and levulose (invert sugar); synaptase, from seeds of the rose order, converts amygdalin into benzaldehyd, hydrocyanic acid and sugar; myrosase (myrosin) exists in both the mustard seeds and hydrolyzes the albuminoids present therein, forming allyl sulfocyanid (volatile oil of mustard); papayotase, found in the juice of papaw (*carica papaya*), converts proteids and starch into soluble compounds; bromelase (bromelin), found in the juice of pineapple fruit, digests proteids; rennase (rennin), found in the gastric juice of the fourth stomach of the calf, coagulates milk, rendering some caseinogens soluble, while precipitating others: these are respectively known as "wheys" and "curds"; catalase, found in tobacco leaves, is an oxidizing enzym which causes fermentation in fresh tobacco leaves, and is productive of the so-called "bouquet of tobacco," which is absent in the fresh leaves.

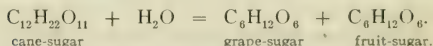
As there are different kinds of ferments, they also cause different kinds of fermentation with different products. The principal kinds of fermentation of interest to the pharmaceutic student are the *alcoholic* or *vinous fermentation*, produced by a vegetable ferment, zymase, which is found in ordinary yeast. The products of its action are alcohol and carbon dioxid.

Acetic Fermentation.—This is caused by a peculiar

vegetable ferment (*mycoderma aceti*) which acts upon alcohol, converting it into acetic acid.

Lactic Fermentation.—This is caused by a vegetable ferment (*bacterium acidi lactici*) contained in sour milk, which has the power of converting sugar into lactic acid.

The germs of various ferments are found in the air, and under favorable conditions they develop and produce their characteristic changes. Such ferments develop, for instance, in a solution of grape-sugar, commonly known as glucose, and if this contains any nitrogenous body which is essential to their development, they will convert the glucose into alcohol and carbon dioxid. The ordinary sugar, which we call “cane-sugar” or “sucrose,” is not directly fermentable. It must first be converted by a nitrogenous substance, which is known as “invertase” and which is invariably a constituent of yeast, into grape-sugar, or glucose, and fruit-sugar, or fructose. This change may be expressed in the following reaction:



The above chemical change or decomposition, in which the elements of water were added to effect the reaction, is known as *hydrolysis*. Invertase, therefore, is a “hydrolytic ferment” or “enzym.” Either of these two sugars so produced (fructose and glucose) are directly fermentable with yeast, forming the alcohol and by-products. It may be added that the reaction expressing the formation of alcohol from

glucose is not as simple as it may appear at first sight; for, in addition to the alcohol and carbon dioxid produced, two amyl alcohols are produced which, together, constitute the "fusel oil"; propyl and isobutyl alcohol, a little succinic acid and about 2.5% of glycerin are formed at the same time.

Manufacture of Alcohol and Beverages.—The grain, which may be either maize, rye, rice, oats, potatoes or other starch-rich fruits (molasses is frequently used) is ground to a meal and macerated in water at a temperature between 85 and 88° C. This process is called "mashing," in which the starch is changed into soluble form, such as dextrose or maltose. This, upon the addition of malted barley or rye, at a temperature of 60° C., is converted by the action of diastase into glucose. This liquid is cooled to about 18° C., yeast is added and the glucose is broken up into carbon dioxid, which is evolved and escapes, and alcohol, which remains in the liquid. Other products formed at the same time are, as said before, propenyl, propyl, isobutyl and amyl alcohols, together with succinic acid. These latter are less volatile; that is, have a higher boiling-point than the ordinary alcohol, which is obtained by fractional distillation. This distillation is best conducted in a "columnar still," best known as "Coffey's still." The ordinary alcohol, besides the admixture of the above alcohols, also contains much water, from which it may be separated by fractional distillation. It, boiling at 78° C., is separated from the water readily, while the fusel oil is separated partly by distillation,

and the last traces of it by filtering the alcohol through animal charcoal. Animal charcoal has the property of absorbing foreign odors and the process is, therefore, known as "deodorization." The water cannot, however, be completely removed by redistillation, though a product containing about 96% of alcohol may be obtained by that process.

Absolute alcohol is prepared from ordinary alcohol by removing the water from it by means of some dehydrating agent, such as quicklime or anhydrous copper sulfate. Thus, by repeated treatment with lime, the water can be reduced to 0.5%, and this small quantity can be further removed by treatment with metallic sodium. The commercial varieties of absolute alcohol contain about 99%. The Pharmacopœia recognizes three forms of alcohol—the ordinary alcohol, containing 92.3% by weight or 95% by volume of absolute alcohol; the absolute alcohol (alcohol absolutum U. S. P.), which should contain not more than 1% by weight of water; and the diluted alcohol (alcohol dilutum U. S. P.), containing 41% by weight or 49% by volume of absolute ethyl alcohol.

The requisites for successful fermentation are

(1) Glucose,	100.0 parts
(2) Albuminoids,	1.0 parts
(3) Mineral salts,	0.5 parts
(4) Yeast,	0.5 parts
	<hr/>
	102.0 parts

(5) Air, at the outset.

(6) A temperature between 5 and 30° C.

And the products of fermentation may be tabulated as follows:

(1) Ethyl alcohol,	48.5 parts
(2) Carbon dioxid,	46.5 parts
(3) Glycerin,	3.6 parts
(4) Succinic acid,	0.7 parts
(5) Fusel oil and extractives,	0.7 parts
(6) Yeast, increased to	2.0 parts
	102.0 parts

(7) Traces of organic esters which give the fermented product its "bouquet."

Beer Manufacture.—Barley is moistened with warm water, strewn upon warm floors and allowed to germinate (sprout). During this process a ferment, called diastase, is developed which converts part of the starch into sugar. The barley is now dried quickly to prevent further growth, and it constitutes the so-called "malt." This malt is ground to a meal and placed in water at about the temperature of 76° C., to allow the diastase to act on the unaltered starch. The liquid is then strained and is now called "wort," to which hops are added to give it the bitter taste and flavor. Yeast is now mixed and the fermentation is allowed to proceed to a certain point, but never to a completion. The yeast is then separated and the beer is drawn off into casks and subjected to high chilling "vatting," in which process the yeast which remains floating, deposits and becomes dormant. The best process for fermentation is dependent upon the correct mainte-

nance of the temperature. Thus, in the United States, a temperature of between 15 and 16° C. is maintained, and the same may be said of Great Britain, while in France and Germany the temperature is not permitted to exceed 12° C. Good beer should not contain alcohol in excess of 3% , and bock beer in excess of 4% .

Lager.—This is a beer brewed at a temperature between 5 and 10° C. This low temperature keeps the yeast at the bottom and hence the fermentation is much more complete. Lager contains between 5 and 7% of alcohol.

Ale.—In the manufacture of ale the temperature is maintained comparatively high—between 15 and 30° C. The bubbles of carbon dioxide rise and carry the yeast to the surface, forming there a thick scum. This mechanically checks the oxidation and hence the fermentation. After the ale has been drawn off into the casks the fermentation starts up again and continues for some time.

Whisky Manufacture.—Whisky is usually made from corn, but frequently from rye, wheat, potatoes or other starch-bearing vegetables. The grain is ground to a meal and mixed with water and a very little malt. This latter furnishes the diastase necessary to convert the starch into sugar. This mixture, called "mash," is kept at a warm temperature until all the starch has been acted upon. The liquid is then drawn off and mixed with the yeast. It is allowed to ferment as much as possible, for it is desirable to get all the alcohol that can be obtained.

It is next distilled and the distillate constitutes the raw whisky, commonly called "high wine." High wine contains alcohol and water in nearly equal proportions. Its strength is designated by the number of "proof degrees" by the United States Internal Revenue Bureau: two proof degrees being equal to 1% by volume of absolute alcohol. The whisky employed for medicinal purposes (*spiritus frumenti* U. S. P.) should correspond to an alcoholic strength of 44 to 55% by volume and stand in barrels not less than four years. During this standing in barrels, whisky is mellowed, developing a number of esters which increase and enhance its bouquet, and such mellowed whisky is called "old whisky."

Rectification is the purification of alcohol and strong alcoholic liquors by the removal of water and fusel oils, chiefly by distillation. Ethyl alcohol volatilizes at a lower temperature than these, and by carefully regulating the temperature at a certain point, these by-products will be left behind in the body of the still.

Wines.—Wines may be said to be the fermented juice of grapes. When grapes are expressed and with their skins permitted to stand at a temperature not exceeding 30° C., they ferment, giving rise to red wines. If the juice, however, has been strained off from the skins before the fermentation sets in, white wines will be the product. If fermentation is permitted to proceed to almost completion, "dry" wines are obtained. These are subjected to distillation and all but about 7% of their alcohol is removed by dis-

tillation. The alcohol so removed possesses a flavor and a bouquet peculiar to itself, and when obtained from champagne grapes is termed "cognac"; but when obtained from the ordinary grape it is termed "brandy." Brandy is, therefore, the liquor obtained by distilling wine (*spiritus vini gallici* U.S.P.), containing from 46 to 55% of alcohol by volume, and at least four years o'd. When the fermentation is not permitted to continue to completion, sweeter wines are produced. These sweeter wines, of which port, angelica and sherry are the types, contain upward of 18% of alcohol, whereas the dry wines, such as claret or hock, contain 7 and 9%, respectively.

Rum is made from molasses by fermentation and distillation.

Gin is made by macerating crushed juniper berries in 60% alcohol and then subjecting to distillation.

Other beverages, such as porter, which may be said to be "evaporated beer," we shall not treat of.

DECAY.—It is well known that many moist organic substances when exposed to the air undergo a slow process of oxidation, and so are gradually destroyed without sensible rise of temperature. This process of slow combustion or oxidation differs from fermentation, and is called *decay*.

Properties of Ethyl Alcohol.—Ethyl alcohol is a colorless, transparent, mobile liquid of a characteristic agreeable odor and burning taste. It boils at 78° C. and has a specific gravity of 0.809 (25° C.). It is miscible with water, ether, chloroform and, with the exception of water, it is the most generally employed solvent in pharmacy. It is one of the best

solvents for resins, alkaloids, essential oils, camphor, iodine and many organic and inorganic compounds. It does not dissolve the fixed fats. It is very inflammable. Its most common impurity is aldehyde. The presence of aldehyde is detected by the addition of silver nitrate which produces discoloration; oak tannin in presence of potassium hydroxide T. S. gives a brownish-yellow color. When 25 c.c. of alcohol are evaporated spontaneously, the barely moist surface of the dish should not be colored red or brown, with 5 drops of concentrated H_2SO_4 which shows the absence of fusel oil and organic impurities.

Chemical Properties of Ethyl Alcohol.—Alcohol may be detected by warming it with a little iodine and potassium hydroxide, when crystals of iodoform will separate and can be identified by their smell and crystalline form. With chlorine it forms chloral, and with bleaching powder and water, chloroform. With strong nitric acid it evolves ethyl nitrate. When it is mildly oxidized, it is converted into acetaldehyde; and if subjected to strong oxidation, it is converted into acetic acid. With chromium trioxide alcohol ignites spontaneously and burns to carbon dioxide and water. When treated with sulfuric acid, it forms ethyl sulfuric acid, commonly known as "sulfovinic acid." If, however, an excess of alcohol is heated with sulfuric acid, ether is formed by the abstraction of water, the acid simply acting as a dehydrating agent.

Adulteration of Ethyl Alcohol and Alcoholic Beverages.—Frequently, for the purpose of reducing the cost of beverages and more frequently in reducing

the cost of remedial agents for external application, and of those given in but small doses, part or all of the ethyl alcohol is substituted by methyl alcohol. In the first instance it is sophistication; in the second instance, substitution. To detect the presence of ethyl alcohol in such mixtures the following method can be employed to advantage:

The alcohol or a solution of it is subjected to distillation and the portion distilling between 60 and 80° is collected. A spiral of copper wire is heated to redness and plunged into the liquid several times, after which it is filtered. One drop of a 0.5% aqueous resorcinol solution is added, and the mixture is floated upon concentrated sulfuric acid. A rose-red zone at line of contact indicates ethyl alcohol; a scanty white or pinkish coagulum appears directly above the zone and finally separates and rises in purplish flakes (similar reactions are given by the tertiary butyl alcohols and formic acid, but the succession of colors and the deportment of flaky coloring matter are different).

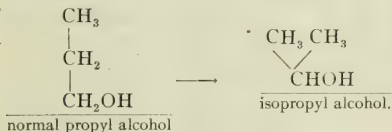
Nomenclature of the Alcohols.—It is sometimes desirable to consider all of the alcohols as derivatives of methyl alcohol—Carbinol. This greatly facilitates the naming of the alcohols. Thus:

Carbinol is methyl alcohol,	CH_3OH
Methyl carbinol is ethyl alcohol,	$\text{CH}_3\text{CH}_2\text{OH}$
Ethyl carbinol is propyl alcohol,	$\text{C}_2\text{H}_5\text{CH}_2\text{OH}$
Dimethyl carbinol is isopropyl alcohol,	$\text{C}_3\text{H}_7\text{CHOHCH}_3$
Propyl carbinol is butyl alcohol,	$\text{C}_3\text{H}_7\text{CH}_2\text{OH}$
Trimethyl carbinol is isobutyl alcohol,	$(\text{CH}_3)_3\text{COH}$
Isopropyl carbinol is primary isobutyl alcohol,	$\text{C}_4\text{H}_9\text{CH}_2\text{OH}$

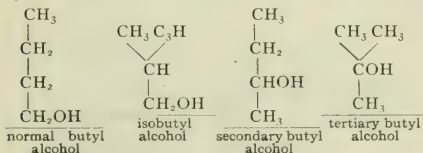
Isomerism among the Alcohols.—The possibili-

ties of isomerism among the alcohols are even greater than among the hydrocarbons. Thus it may arise in three ways: (a) by branching of the carbon chains; (b) by changing the position of the hydroxyl group; (c) or through both of these simultaneously. Thus, while methyl and ethyl alcohols have no isomers, there are two propyl alcohols, the normal and the iso-; four butyl alcohols; eight amyl alcohols, etc.

The Propyl Alcohols.—Normal propyl alcohol has a boiling-point of 97.4° and may be separated from fusel oil by fractional distillation, while isopropyl alcohol boils at 82.7° and is obtained by acting on acetone with sodium amalgam. The following are the graphic formulas of the two propyl alcohols:



The following are the graphic formulas of the four butyl alcohols:

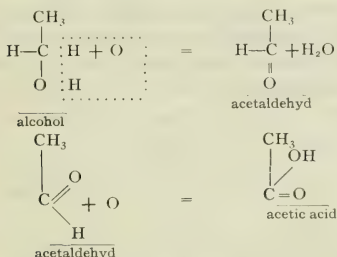


The Effects of Oxidation Upon the Alcohols.—It has been said that primary alcohols upon oxidation yield aldehyd, and when subjected to still further oxida-

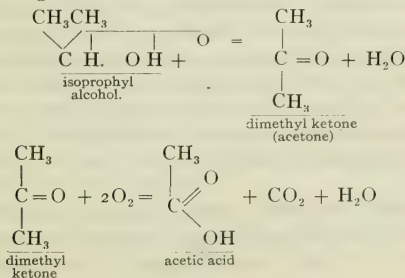
TABLE OF ISOMERIC ALCOHOLS.

Name.	Formula.	Boiling-point.	Specific gravity at 20°
Propyl Alcohols, C_3H_8O :			
(1) Normal,	$CH_3-CH_2-CH_2-OH$	97°	0.804
(2) <i>Is</i> o,	$CH_3-CHOH-CH_3$	81°	0.789
Butyl Alcohols, $C_4H_{10}O$:			
(1) Normal primary,	$CH_3-CH_2-CH_2-CH_2-OH$	117°	0.810
(2) Normal secondary,	$CH_3-CH_2-CHOH-CH_3$	100°	
(3) <i>Is</i> o,	$(CH_3)_2-CH-CH_2OH$	107°	0.806
(4) Trimethylcarbinol,	$(CH_3)_3-C-OH$	83°	0.786
Amyl Alcohols, $C_5H_{12}O$:			
(1) Normal primary,	$CH_3-(CH_2)_3-CH_2OH$	138°	0.815
(2) <i>Is</i> o butylcarbinol,	$(CH_3)_2-CH-CH_2-CH_2OH$	131°	0.810
(3) Secondary butylcarbinol,	$CH_3-CH(C_2H_5)-CH_2OH$	128°	
(4) Methylpropylcarbinol,	$CH_3-(CH_2)_2-CHOH-CH_3$	119°	
(5) Methylisopropylcarbinol,	$(CH_3)_2-CH-CHOH-CH_3$	112.5°	
(6) Diethylcarbinol,	$C_2H_5-CHOH-C_2H_5$	117°	
(7) Dimethylethylcarbinol,	$(CH_3)_2-C(OH)-C_2H_5$	102°	
(8) Tertiary butylcarbinol,	$(CH_3)_3C-CH_2OH$	112°	

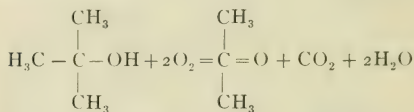
tion, they yield acids. The following reactions demonstrate this fact:



The secondary alcohols in the first stage of oxidation also lose 2 atoms of hydrogen, but the resulting compounds are termed "ketones." Thus secondary propyl alcohol (iso-) upon oxidation yields dimethyl ketone, commonly known as acetone. Ketones upon further oxidation split up into acids having fewer carbon atoms, carbon dioxid and water. The following reactions illustrate this:



When tertiary alcohols are oxidized they form ketones or acids with fewer carbon atoms than the original alcohol contained. Thus the tertiary butyl alcohol containing 4 carbon atoms splits up into dimethyl ketone (containing three carbons), carbon dioxid and water, as the following reaction illustrates:



The nature of the alcohols may be determined by still another process than the oxidation method. The oxidation method is somewhat tedious and a "color-test diagnosis" has been recommended. (Victor Meyer.)

The alcohol is converted into alkyl halid by treatment with red phosphorus and iodine; the iodid is dried with calcium chlorid and then distilled with silver nitrite. A nitroparaffin is obtained which is mixed with potassium nitrite and dilute potassium hydroxid. Dilute sulfuric acid is next added drop by drop. If this produces a *red color* it indicates a *primary alcohol*; a *blue color* points to a *secondary*; while *no coloration* indicates a *tertiary alcohol*. (This test is sometimes called "the red, blue and white test.")

AMYL ALCOHOL, pentyl alcohol, $\text{C}_5\text{H}_{11}\text{OH}$. This alcohol derives its name from *amylum*, starch. Two of its eight isomerids constitute the so-called

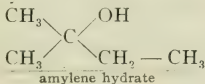
fusel oil. Fusel oil is a mixture of the secondary butyl carbinol and isobutyl carbinol, has a characteristic, unpleasant odor and is not miscible with water, but floats upon it like an oil, from which it derives its name "fusel oil." Fusel oil is obtained from high wine, but the glucose obtained from potato starch yields a considerably greater amount of it, and hence amyl alcohol is sometimes known as "potato oil."

Properties.—Commercial amyl alcohol is an oily, yellowish liquid which, when oxidized, yields *valeric acid*.

AMYL NITRITE, $C_5H_{11}NO_2$, is prepared by a process similar to that employed in the making of ethyl nitrite; that is, by distilling a mixture of the alcohol, sodium nitrite and sulfuric acid. Amyl nitrite is a highly aromatic substance, has a low boiling-point and should consist of at least 80% of isoamyl nitrite (amylis nitris U. S. P.)

AMYL ACETATE, $C_5H_{11}-C_2H_3O_2$. This ester is prepared by distilling a mixture of amyl alcohol, sodium acetate and sulfuric acid. It constitutes the jargonelle pear essence. Mixed with methyl alcohol and benzin, it constitutes the so-called "banana oil" of the painters, used to suspend aluminum and gold bronzes for painting.

AMYLENE HYDRATE, ethyl dimethyl carbinol, is used as a hypnotic $(CH_3)_3C \cdot CH_2OH$. On oxidation it yields only acetic acid:

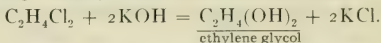


CHAPTER XXV.

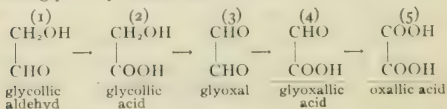
DIATOMIC ALCOHOLS OR GLYCOLS.

THE alcohols of the olefins or the ethylene series are all diatomic or diacid. They contain two hydroxyl groups in the molecule, they are heavy and viscid, reminding one of glycerin, and hence the name "glycols" is applied to the group. The glycols are not very interesting to the pharmacist.

Properties.—The glycols can be easily prepared from the dihalogen derivatives of the olefins by the action of water and a metallic oxid in much the same way as the monatomic alcohols are obtained by treating the alkyl halids with an alkali; thus:

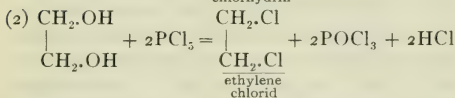
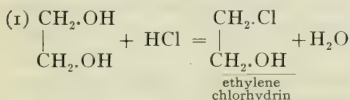


The glycols are colorless, viscid liquids with a high boiling-point. Thus, ethylene glycol boils at 195°C . They are all very soluble in water. The glycols exhibit all the properties of the alcohols, but doubly. Thus, ethylene glycol contains two primary alcohol groups, and by successive oxidation of these groups to aldehyd and carboxyl groups, the following series of products should be derivable. However, only the second, third and fifth have been obtained from glycol by oxidation.

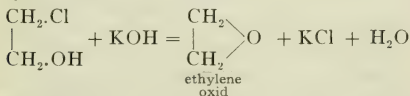


Among the more interesting compounds of ethylene glycol the following may be mentioned:

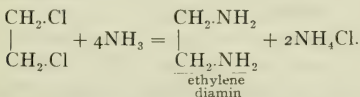
When hydrochloric-acid gas is passed into glycol, one of its hydroxyls is replaced by the chlorin, forming a chlorhydrin and splitting off water. When, however, glycols are treated with phosphorus pentachlorid, both hydroxyls are replaced, and ethylene chlorid is formed; thus:



When caustic alkalis act upon chlorhydrins, "ethylene oxids" are formed:

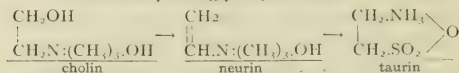


When ammonia gas acts upon ethylene chlorid, it replaces the chlorin with two amido groups and forms diamin:



This is a primary diamin, with basic properties of theamins.

Cholin, *neurin*, *taurin*, may all be said to be derivatives of ethylene glycol; thus:

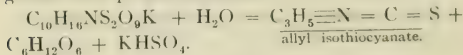


Cholin is found in the brain and egg-yolk, forming with glycerol, stearic and phosphoric acids a complex compound—lecithin ($\text{C}_{45} \text{H}_{83} \text{N}_3\text{O}_9\text{P}$). *Neurin* is a product of the putrefaction of albumin, and classed among the ptomaines. *Taurin* is a constituent of bile.

The second of the olefinic alcohols is *allyl alcohol* $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$. It is derived from the second member (propylene) of the olefin hydrocarbons, and is prepared by heating isopropylene, allyl iodid ($\text{C}_3\text{H}_5\text{I}$) with water at 100° . The isothiocyanate of this alcohol constitutes the *essential oil of mustard*, and the sulfid constitutes *oil of garlic*:



In nature, the oil of mustard (essential) is obtained by macerating ground black mustard seeds with cold water and distilling the product with steam. The potassium myronate—a glucosid of the seeds—is fermented by myrosin, an enzym present, and the oil, glucose and potassium bisulfate are formed; thus:

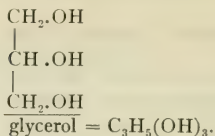


TRIATOMIC ALCOHOLS OR GLYCERINS.

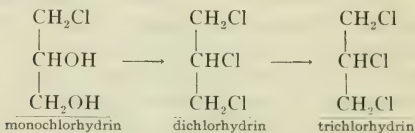
As the monatomic alcohol CH_3OH corresponds to the inorganic hydroxid NaOH , and the diatomic glycol $\text{C}_2\text{H}_4(\text{OH})_2$ to the inorganic calcium hydroxid $\text{Ca}(\text{OH})_2$, so do the triatomic alcohols, as glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, correspond to ferric hydroxid, $\text{Fe}(\text{OH})_3$.

GLYCERIN, glycerol, propenyl alcohol, is a clear, odorless, colorless, sweet liquid, having the specific gravity 1.246 and a boiling-point of 290° . It cannot be distilled alone, but it is readily distilled with superheated steam under reduced pressure. It is very hygroscopic, neutral, and dissolves in water and alcohol, but is insoluble in chloroform, benzol and the fixed oils. It was discovered by Scheele (1779), who isolated it while making lead plaster; and Chevreul found it to be the constituent of natural fats and oils. It can be prepared from fats by saponification, by decomposing these with caustic alkalis; also by passing superheated steam through a fat. This last method is the one most commonly used in the manufacture of glycerin. Glycerin does not freeze until about -17° , and for that reason it is valued in gas meters and automobiles which must be exposed to low temperatures. Large quantities of it are employed in the manufacture of glyceryl nitrate (nitroglycerin), from which, in turn, dynamite is made. In pharmacy it is used as a solvent. Its graphic formula shows it to be composed of three alcoholic groups, of which one is secondary and two are primary:



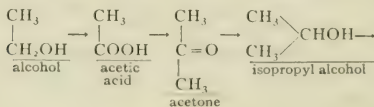


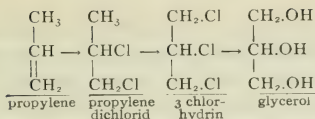
Chemical Properties of Glycerin.—When heated with sulfuric acid, acrolein is formed, which is recognized by its odor. It liberates boric acid from borax. With chlorin it forms *mono*-, *di*- or *tri*-*chlorhydrins*:



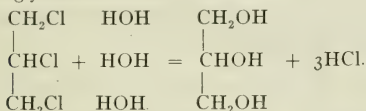
Glycerin should not reduce Fehling's solution, showing the absence of glucose (its frequent adulterant). Glycerin dissolves coloring matters, tannin and extractives, and may be called an "intermediate" solvent between alcohol and water. It increases specific gravity of fluid extracts and tinctures, preventing their precipitation.

Structure.—The structure of glycerol has been determined by several syntheses, of which the following one may be given as an example:

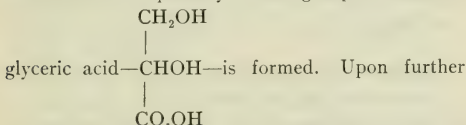




When acetone is reduced, isopropyl alcohol is formed which, when heated with sulfuric acid, forms propylene. Propylene, in turn, combines with chlorine, giving propylene chlorid which, when treated with iodine chlorid, is converted into trichlorhydrin. Trichlorhydrin, heated with water to 170° , yields glycerol:



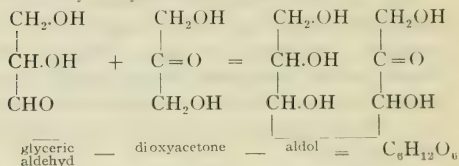
When glycerol is reduced with hydrogen, the secondary group is attacked, giving rise to dioxyacetone, $\text{CH}_2\text{OH} - \text{CO} - \text{CH}_2\text{OH}$. Allyl alcohol (found in oil of garlic), when oxidized with potassium permanganate, yields glycerol. The trivalent radical of glycerin is sometimes termed "glyceryl." When one of the primary alcohol groups is oxidized,



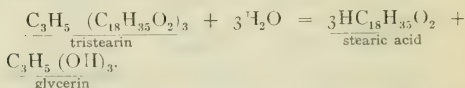
oxidation, the second primary alcohol group is affected, and tartronic acid is formed. When dioxyacetone is treated with caustic soda, it is con-

verted into glyceric aldehyd, which condenses with part of the dioxyacetone, giving rise to an artificial sugar which, chemically, is an inactive fructose (a-acrose), to which the name *aldol* has been given.

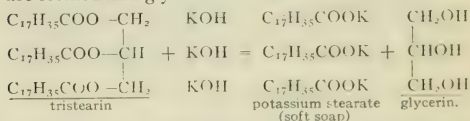
Aldol may be synthetized as follows:



Manufacture of Glycerin.—(1) By superheating stearin with water:



(2) As a by-product in the manufacture of soap. When fats are boiled with an alkali hydroxid, *soaps* are formed and glycerol is set free:

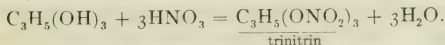


From the above it will be seen that *soaps*—sodium or potassium oleate or stearate—are *salts of the fatty acids*. Potassium stearate is very deliquescent. It takes up water from the air and is, therefore, termed “soft soap”; sodium stearate is not deliquescent and constitutes the hard soaps of the market. Some

salts of these acids, such as calcium or magnesium, are insoluble in water, and they must all be precipitated before the soap will act as a detergent. This is the reason why the use of soaps in laundering is attended with great waste of soap. Hard waters for laundry purposes may be rendered soft by precipitating these compounds and decanting the so-softened water. One method of accomplishing this is to add about one grain of alum per each gallon of water, stirring it well and letting it stand for some little time, when the aluminum hydroxid and carbonate formed therein will slowly subside, carrying with it all of the inorganic "hardening salts" in solution, in the water.

Glycerol forms salts with nitric acid, of which the trinitrate is the most important.

Trinitrin, nitroglycerin, glonoin, Nobel's oil, $C_3H_5(ONO_2)_3$. Trinitrin was discovered by Sobrero (1841), but was first applied practically by Nobel (1867). Nitroglycerin is prepared by mixing 12 parts of fuming nitric acid with 20 parts of sulfuric acid, and running into this well-cooled mixture a very thin stream of glycerol, which is forced in by a current of air. The sulfuric acid serves here as a dehydrating agent:



The mixture is diluted with water, the nitroglycerin separates in oily drops or layer, which is carefully washed with water to separate the glycerin, and next with a weak solution of soda to free it from

the acids. It is then converted into the many explosive compounds.

This highly explosive compound has the appearance of a yellowish oil, which is highly volatile.

By warming nitroglycerin carefully and dissolving in it collodion-cotton (nitrocellulose); upon cooling, the mixture solidifies to a jelly-like consistence. This jelly is insoluble in water and is well adapted to many purposes where explosives are required. It is called *explosive gelatin* or *blasting gelatin*.

Dynamite is made by mixing 3 parts of nitroglycerin with 1 part of a fine silicious earth, such as kieselguhr, which is very porous and which can absorb considerable quantities of nitroglycerin without becoming pasty. This mixture is moulded into cartridges or sticks and fired by a detonator, usually made of mercury fulminate. When gun-cotton and nitroglycerin are made into a pulp with acetone and a little petrolatum, *cordite* is formed. This pulp is squeezed through small holes into tiny threads which, upon evaporation of the acetone, are used after being cut up for smokeless rifle cartridges. When mixed with sawdust, nitrate of potassium or ammonium nitrate, various explosives are formed which are known under such names as *porcite*, *vulcan powder*, etc. The method of manufacture of trinitrin is similar to the formation of ethyl nitrate from ethyl alcohol, and, like the latter, it can be saponified by caustic alkalis, showing that in fact it is an ester and not a nitro compound. The name nitroglycerin, therefore, is only used because through usage it has

been adopted as the technical name of the compound, but in fact it is a misnomer. Nitroglycerin is official in the Pharmacopœia as a spirit (*spiritus glycerylis nitratis* U. S. P.), which contains 1% by weight of nitroglycerin.

THE FATS.

In constitution the fats resemble nitroglycerin in that they are esters of the higher fatty acids. Thus, olive oil, cottonseed oil and expressed almond oil are chiefly glyceryl esters of oleic acid; palm oil is chiefly glyceryl of palmitic acid; beef tallow is nearly pure glyceryl stearate, while castor oil is glyceryl ricinoleate; expressed oil of nutmeg (nutmeg butter) is chiefly glyceryl myristate. Again, expressed laurel oil is glyceryl laurate and butter is glyceryl butyrate. These glyceryls are the proximate principles of these various fats and are collectively known as fats. The important fats are:

Laurin, $C_3H_5(C_{12}H_{23}O_2)_3$, its acid = $HC_{12}H_{23}O_2$ = lauric acid.

Myristin, $C_3H_5(C_{14}H_{27}O_2)_3$, its acid = $HC_{14}H_{27}O_2$ = myristic acid.

Palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, its acid = $HC_{16}H_{31}O_2$ = palmitic acid.

Olein, $C_3H_5(C_{18}H_{33}O_2)_3$, its acid = $HC_{18}H_{33}O_2$ = oleic acid.

Stearin, $C_3H_5(C_{18}H_{35}O_2)_3$, its acid = $HC_{18}H_{35}O_2$ = stearic acid.

Liquid fats consist almost entirely of olein; olive oil, cottonseed oil and expressed oil of almonds are

examples of pure olein. They are sometimes called fatty or *fixed* oils, to distinguish them from the essential, volatile or ethereal oils.

Solid fats contain a larger proportion of palmitin and stearin; it might be said that the relative proportion of each of the three glyceryls (palmitin and stearin are solids, olein a liquid) present in the fat determines its consistency and other physical properties.

Composition.—The animal fats consist principally of about 80% of the glyceryl esters of the higher fatty acids (stearic, palmitic and oleic) and about 20% of the esters of the lower fatty acids and sometimes the esters of the higher alcohols. The proportion of these esters varies with the sources of the fats.

Properties.—The solid fats melt below 100°C . and can be distilled at about 300°C . with a slight decomposition. At higher temperatures they are decomposed into *acrolein*. When pure they are colorless, odorless and tasteless. They are insoluble in water, sparingly in cold alcohol, but freely in ether, chloroform, benzene and carbon disulfid. They all have a lower specific gravity than water. Upon standing, by a decomposition peculiar to the fats alone and due perhaps to oxidation or fermentation (and maybe to both), fats acquire color and taste. These are, therefore, products of decomposition. The disagreeable odor and taste of fats (rancidity) is due to the fatty acid which is liberated. Such rancid fats, when heated with sodium carbonate solution, are deprived of their disagreeable odor.

The liquid fats all have a specific gravity lighter than water, but when exposed to lower temperatures, they become partly solid (lard oil), and through such reduction of temperature some of the principles may be separated from the others.

Preparation.—Animal fats are prepared from the tissues by melting them alone or in the presence of water and separating the fused fat by straining. Many of the vegetable oils are prepared by expression, sometimes by extraction with a volatile solvent, such as petroleum benzin, carbon tetrachlorid, etc., while inferior oils are obtained by boiling the material with water, decanting the floating oil from the refuse matter and straining.

Adulteration.—Fats are very prone to adulteration with commoner or cheaper varieties. Owing to the similarity in composition, the adulterants are difficult to detect. The principal means of detection of the fraud is by the odor, which is peculiar upon warming, by the color reaction with acids or silver nitrate and by the boiling- and melting-points. Fish oils (a frequent adulterant) are detected in the vegetable oils by passing chlorin gas through the oil. In the presence of *fish* oils, the fat will turn *dark*. Sulfuric acid, when heated with ten parts of the oil, produces different colorations, depending on the nature of the oil, and serves as a means of identifying the same. Thus, with oil of black mustard, a bluish-green color is acquired; with fish oil, a reddish color; and with linseed oil, a dark brown. The identity and purity of fats may be determined quantitatively by the

"saponification value." This depends upon the number of cubic centimeters of alcoholic potash required to neutralize a weighed quantity of the oil. The other test is the determination of the "iodin number," which depends on the determination of the percentage of iodine solution absorbed by the fat.

In the case of vegetable fats, the presence of protein or mucilaginous substances tends to rancidify them. These impurities may be removed by filtration or by treatment with 2% sulfuric acid. The acid is gradually added to the fat in which it carbonizes the impurities and, after separating the acid and repeated agitation with water to wash away the last traces of it, the fat is subjected to filtration.

Fats should be preserved in perfectly dry, hermetically sealed vessels and in a cool place.

Beef tallow, mutton suet and lard are mixtures of stearin, palmitin and olein. In the first fat, stearin predominates; and in the last fat, olein.

Butter is a complex mixture of the glycerids of butyric, caproic, caprylic, capric, myristic, palmitic and stearic acids. The first four of the above esters constitute about 12% of butter. They are volatile with water vapor and can be separated from the other constituents of butter by distilling with steam. Butter is made from the cream of cow's milk by the process of churning. When of good quality, it should contain about 90% of fat, 8% of water, 1% of curd and 1% of salt. As said before, butter consists mainly of stearin, with about 7% of butyrin. The

purity of butter may be roughly determined by saponifying a weighed quantity with caustic soda, acidifying with sulfuric acid and distilling. The volatile fatty acids which distill over are estimated by titration with alkali hydroxids. The water is determined by drying a weighed sample of butter in a hot-water oven to a constant weight. The salt and curd may be determined by melting and passing through a weighed filter, washing the filter with ether until free from fat. The curd and salt remain upon the filter, and the salt is estimated by igniting the filter, burning off the organic matter, and the curd by difference. Old, rancid butter may be deprived of its rancidity by heating it and treating with a solution of sodium carbonate and afterward by kneading it with sweet milk, which latter serves two purposes: first, to wash away the traces of the alkali present, and, second, to impart a sweet-milk flavor to the butter. Such is the method of making "renovated butters."

Renovated butters may be readily detected by heating them slightly in a test-tube, when the rancid odor will at once appear; and upon higher heating, a frothing will occur with a peculiar, crackling sound. Since, as an article of diet, butter is rather high-priced, many so-called "butter substitutes" have been offered. Of these *margarin*, *oleomargarin*, *butterin* and *cottosuet* are the familiar commercial examples. These are prepared by melting beef tallow or suet and heating to a temperature of 35° and subjecting to pressure. The lower melting portion, which is expressed, contains a large quantity of olein, to which

the name "oleo oil" has been given. This, when mixed with cottonseed oil and a little milk and genuine butter, upon chilling, constitutes oleomargarin. The butter substitutes can be identified by the fact that the volatile fatty acids (butyric acid) are always considerably below that of the genuine butter (4-5.5%). The melting-points of the two articles also vary considerably. When properly prepared, margarin is a perfectly wholesome article of food and in chemical composition very similar to butter.

Wool-fat, also called wool-grease, Yorkshire grease, and its purified varieties, known under the fanciful name of "lanolin" (adepts lanæ, and adepts lanæ hydrosus U. S. P.), constitute the official fat from sheep's wool. It is prepared by scouring wool. Chemically, it is a complex mixture of the fatty acids with *cholesterol*, an alcohol having the formula $C_{26}H_{44}O$. It is separated from the wool washings by adding sulfuric acid, which causes the "cracking," or raising the greasy matter to the surface, when it is skimmed off. It comes into the market in a brown, semi-solid mass which, upon trituration with water, forms a straw-colored emulsion known as the hydrated wool-fat or "lanolin." The cholesterol is capable of absorbing more than its own weight of water, it resists saponification and does not rancidify. It has also the property of penetrating the skin and is, therefore, preferable to the other unguents. Cacao butter, obtained by expressing roasted chocolate nuts, is known in pharmacy as a yellowish-colored fat.

melting at 30 to 35° C. to a clear liquid, and having a specific gravity of 0.97. Chemically, it is a mixture of olein, palmitin, stearin, arachin and laurin. It is used for making suppositories and ointments (*oleum theobromatis* U. S. P.).

Liquid fats are classified into:

(a) *Drying oils*; this group embraces poppy, linseed, hemp and nut oils.

(b) *Nondrying oils*; olive, almond, rape, colza, lard, tallow and neatsfoot oils. (The first four are vegetable.)

(c) *Intermediate oils* (which possess some properties of each of the above two classes. These embrace codfish oil, cod-liver oil, sperm, hake, porpoise, shark and whale oils. This is the so-called *fish-oil group*. To the *cottonseed oil group* belong cottonseed oil, sunflower, beechnut and teel oils. Besides, the two alcohol-soluble oils—castor oil and croton oil, are classed here.

All of the above fats when saponified yield soaps and glycerin.

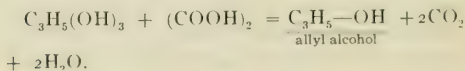
The Waxes.—This is a division of the fats consisting of those which, on saponification, *yield no glycerin*, but do yield complex, monatomic alcohols. All waxes are solid at the ordinary temperature, and they include beeswax, which may be bleached by exposing it to light; Chinese-wax, Brazilnut wax, myrtle wax, palm wax and spermaceti, the last obtained from deposits in the head cavities of the sperm-whale.

Manufacture of Candles.—Stearic acid, which we commonly call stearin, is used in the production of

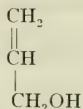
candles. After tristearin is hydrolyzed with superheated steam, pure stearic acid is obtained, this after separation from glycerin, is afterward pressed while hot to remove the liquid oleic acid, and to produce the harder and firmer stearic acid. Stearic acid, after mixing with a little paraffin wax, is moulded into candles. Sometimes paraffin wax with a mixture of but a trace of stearic acid is used for the same purpose.

Varnishes.—Among the drying oils, poppy oil and linseed oil were mentioned. These oils, when exposed to the air, oxidize slowly, forming a hard varnish. The absorption of oxygen from the air by these oils can be made to take place much more rapidly; thus: By boiling the drying oils with lead oxid, manganese dioxid or oxalate, these take up all of the oxygen and are converted into “boiled oils,” also called “quick-drying oils.” When linseed oil is boiled with resins or “varnish gums,” as they are sometimes called, such as kauri gum, copal gum or dammar gum, varnishes are produced. Varnishes are sometimes thinned by turpentine, benzin or alcohol.

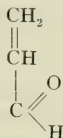
Allied Products.—As glycerin is a product of the fats, so allyl alcohol is also a product of glycerin. When glycerin is heated with oxalic acid, two of the OH groups are removed, according to the following formula:



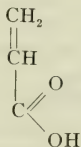
giving rise to *allyl alcohol*, to which the following graphic formula has been ascribed:



When allyl alcohol is subjected to further oxidation, the remaining primary alcohol group is oxidized and an aldehyd called *acrolein* is formed:

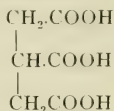


Acrolein is a liquid possessing a pungent odor and is a constituent of the acrid fumes from burning fat. When acrolein is subjected to oxidation, *acrylic acid* is formed, to which the following graphic formula has been ascribed:



When all three hydroxyl groups of glycerin have been replaced by oxidation with COOH groups,

tricarballic acid, to which the following graphic formula has been ascribed, is formed:



This acid is chemically interesting from the fact that its hydroxyl derivative, which has also been obtained from glycerin, is the very important *citric acid*.

CITRIC ACID, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$, exists naturally in the fruits of the members of the orange family, such as lemons, limes, oranges, etc.

Manufacture of Citric Acid.—On a large scale, the lemon peel is first grated off and from it, by solution with petroleum ether, oil of lemon is obtained. The lemons are then sliced, their juice expressed and subjected to boiling. In the process of boiling the albuminous and mucilaginous principles are coagulated and can be removed by filtration. To the filtered aqueous solution lime-water is added, which neutralizes the juice and forms calcium citrate. By adding to the solution of calcium citrate sulfuric acid, the salt is decomposed and citric acid is liberated. It is then subjected to filtration to free the liquid from the insoluble calcium sulfate. The liquid is further evaporated to a small bulk and permitted to crystallize. Citric acid should be carefully examined for the presence of calcium sulfate and free sulfuric acid.

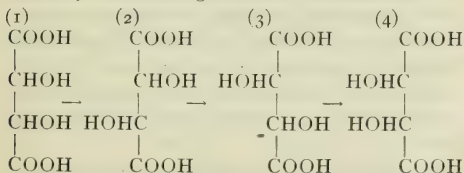
Other Polyatomic Alcohols.—Besides glycerin, another triatomic alcohol is known, namely, pentenyl

alcohol, $C_5H_9(OH)_3$, also called amyl glycerin. *Erythritol*, $C_4H_6(OH)_4$, is a tetratomic alcohol found in certain lichens. It is of little importance, but the dibasic acid corresponding to it is very important.

TARTARIC ACID is a dibasic and diatomic acid and exists in four different physical modifications. The chief difference in these modifications is found in the crystalline form of the salts produced from them and in the behavior of their solution when viewed with polarized light. The four kinds of tartaric acid known are:

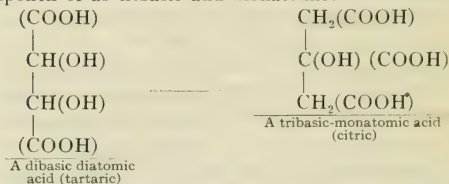
- (1) Dextrotartaric acid (the acid in ordinary use).
- (2) Levotartaric acid.
- (3) Racemic acid (a mixture of equal weights of the dextro- and levo-modifications; inactive, but efflorescent).
- (4) Mesotartaric acid (inactive, and obtained by heating the ordinary dextro acid with a small quantity of water).

The graphic relations of the four acids may be shown by the following structural formulas:



When speaking of tartaric acid we said it was

dibasic and diatomic. The basicity of an organic acid is reckoned by the number of the carboxyl (—COOH) groups it contains, while the atomicity of an acid is reckoned by the number of hydroxyl (—OH) groups it contains in addition to the carboxyl groups. Thus, we observe that the tartaric acids contain in their graphic formulas two carboxyl and two hydroxyl groups and are, therefore, dibasic and diatomic, while citric acid contains three carboxyl groups and one hydroxyl group and is, therefore, spoken of as tribasic and monatomic:



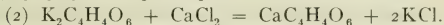
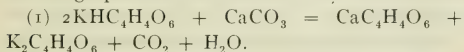
(The different groups will be found in parentheses.)

Tartaric acid occurs in nature chiefly as impure potassium bitartrate, or cream of tartar, commercially known as *argols*. It is deposited during the process of fermentation in the form of a brown, crystalline crust, also called "wine-lees." It was isolated by Scheele (1769), and is found widely distributed in fruits. With malic acid it is found in the berries of mountain ash, and is also found in gooseberries, raspberries, strawberries, its main source being grape juice.

When grape juice is subjected to fermentation, the alcohol which forms in the process renders the

potassium salt of tartaric acid insoluble, and this deposits in minute crystals on the sides and bottom of the vat. The brown powder dissolved in water, filtered through bone-black, the solution evaporated and allowed to crystallize, constitutes "cream of tartar." Both tartaric acid (*acidum tartaricum* U. S. P.) and potassium bitartrate, "cream of tartar" (*potassii bitartras* U. S. P.), are official; the first is required of 99.5%, the latter, 99% purity.

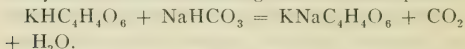
Tartaric acid is prepared from argols by dissolving it in water and neutralizing with chalk. The insoluble calcium tartrate which deposits by filtration is separated from the neutral potassium tartrate which remains in solution. The solution, by being treated with calcium chlorid, gives a further yield of the acid. The entire process is represented in the following equations:



The solution of calcium tartrate is next decomposed by sulfuric acid, filtered from the insoluble calcium sulfate, concentrated by evaporation and allowed to cool, when crystallization will take place. The potassium chlorid is recovered as a by-product and employed in the manufacture of potassium salts. Tartaric acid occurs in large prisms, is freely soluble in water and alcohol and has a melting-point of 135°C . When subjected to dry distillation, *pyro tartaric acid*—(methyl succinic acid,) $\text{CH}_3\text{—CH}(\text{COOH})\text{—CH}_2(\text{COOH})$ —is formed.

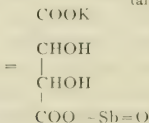
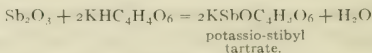
The official salts of tartaric acid are "Rochelle salts" and "tartar emetic."

Rochelle salt is chemically potassium and sodium tartrate—a double salt occurring in transparent prisms or a white powder, soluble in 1.2 parts of water. It is prepared by adding cream of tartar to a solution of sodium bicarbonate. The operation should be carried on carefully, owing to the evolution of carbon dioxide gas, until the first solution is neutralized. It is next filtered, evaporated and allowed to crystallize. The following reaction takes place:



Rochelle salt (potassii et sodii tartras U. S. P.) is an ingredient in the official compound effervescent powder (seidlitz powder). It is sometimes called "Seignette's salt" after its discoverer, Seignette de la Rochelle.

Tartar emetic (antimonii et potassii tartras U. S. P.) is the potassio-stibyl tartrate, an acrid salt, crystallizing with half a molecule of water; soluble in water and prepared by dissolving antimonous oxid in a solution of cream of tartar:



Tartar emetic is a strong poison. The best anti-

dote is tannic acid or any substance containing it.

Baking Powders.—These usually are mixtures of cream of tartar with sodium bicarbonate and starch or other dry material which serves the purpose of a “filler” and acts as an absorbent of any moisture, thus preventing the liberation of any free carbon dioxid. The baking powder is added to flour and stirred with water, forming dough. This operation liberates the carbon dioxid which, in the process of baking, is evolved, making the bread porous and spongy. The reaction which takes place is identical with the one exhibiting the formation of Rochelle salt. Since sodium carbonate is harmful, its excess in baking powders should be carefully avoided. A good baking powder can be made by carefully drying cream of tartar and sodium bicarbonate and mixing these with starch in the following proportions: cream of tartar, 4; sodium bicarbonate, 2; starch, $\frac{1}{2}$ part. Alum is sometimes found a constituent in commercial baking powders, this in the presence of sodium bicarbonate forms the injurious and insoluble aluminum hydroxid with the evolution of carbon dioxid. Alum baking powders should be guarded against.

Calcium diphosphate with sodium bicarbonate frequently forms the addition to the so-called “self-rising” flours.

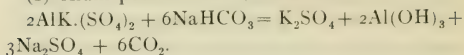
The reactions of the three classes of baking powders:

(1) Cream of tartar with a bicarbonate reacts thus:



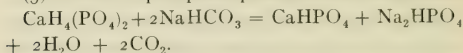
Rochelle salts being formed.

(2) Alum powders react as follows:



Aluminum hydrate and sulfates of sodium and potassium being formed.

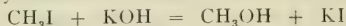
(3) The acid-phosphate powders react as follows:



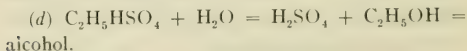
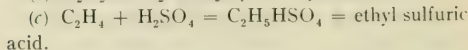
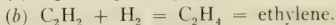
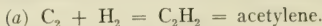
Hydrocalcium phosphate and sodium phosphate are produced in the reaction.

Arabitol and *Xylitol*, $\text{C}_5\text{H}_7(\text{OH})_5$, are both pentatomic alcohols, both obtained by reducing their corresponding aldehyds; arabinose, a constituent of gum arabic; and xylose, a wood gum obtained from various trees by digestion with caustic alkali and precipitation with alcohol. Among the hexatomic alcohols are classed *mannitol*, *dulcitol* and *sorbitol*, $\text{C}_6\text{H}_8(\text{OH})_6$, all found in the different species of ash; they all contain a straight chain of carbon atoms.

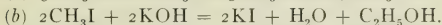
Synthesis of the Alcohols.—(1) Methyl alcohol may be synthetized by treating methyl halid with potassium hydroxid:



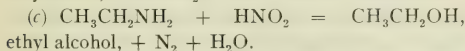
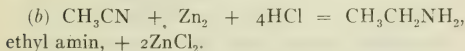
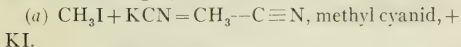
Ethyl alcohol may be synthetized from its elements as follows:



(2) Ethyl alcohol may be produced from methyl alcohol by converting the latter with phosphorus iodid into a methyl halid, two molecules of which treated with two molecules of potassium hydroxid split into two molecules of potassium iodid, water and ethyl alcohol; thus:



A third method of synthesis is by converting the alkyl halids with potassium cyanid, which reaction yields alkyl cyanids, called *nitrils*. When a nitril is treated with zinc and hydrochloric acid, it is reduced to ethyl-amin. This can be diazotized by treating with nitrous acid, yielding ethyl alcohol, water and nitrogen, as follows:

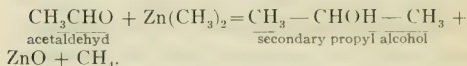


This reaction is a very important one in that we may pass from a one-carbon-atom compound to a two-atom-carbon compound, and from a two-carbon to a three-carbon compound, etc. By this method of synthesis we can build up very complex compounds from simpler ones.

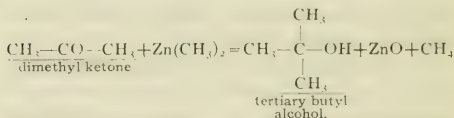
Methyl cyanid may be obtained directly by heating ammonium acetate with phosphorus pentoxid, and for this reason it is frequently called *aceto-nitril*.

Secondary and tertiary alcohols may be synthesized

as follows: When acetaldehyd is heated with zinc alkyl compound, the zinc atom of the latter attaches itself to the oxygen atom by one bond, losing at the same time an alkyl group which, in turn, is transferred to the unsaturated carbon atom of the same group. The product is subsequently decomposed with water, forming the alcohol; thus:



When ketones are treated with zinc alkyl compounds, tertiary alcohols are formed; thus:

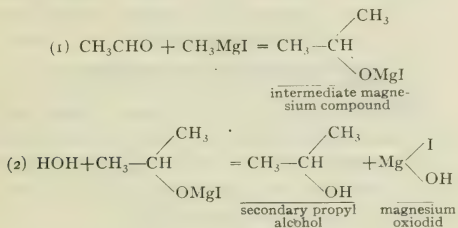


Secondary alcohols may also be synthetized by means of the magnesium alkyl compounds by what is known as "Grignard's reaction." When an alkyl bromid or iodid reacts with magnesium in the presence of ether, corresponding magnesium alkyl bromid or iodid is formed. Thus:



The magnesium alkyl compounds are decomposed by water and form paraffins. With aldehyds ketones and esters, etc., when decomposed with

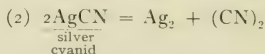
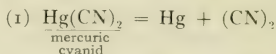
water, they form secondary and tertiary alcohols and ketones; thus:



CHAPTER XXVI.

THE CYANOGEN COMPOUNDS.

CYANOGEN, C_2N_2 (from *kyanos*, blue, and *gennao*, to generate, due to the fact that some of the double cyanids possess a brilliant blue color), was first prepared by Gay-Lussac, who made it by heating either mercuric or silver cyanids:



Cyanogen is a colorless gas with a characteristic odor resembling that of the essential oil of bitter almonds; it is very soluble in water and very poisonous. It is combustible, burning with a pink flame, producing carbon dioxid and free nitrogen. Its specific gravity is 26 and its formula $(CN)_2$ is often written Cy.

Test.—The odor of the gas and the peculiar pink color of the flame serve as the best means for the recognition of cyanogen. Dissolved in water, it forms a very poisonous acid which in its dilute form—2% strong—is official (acidum hydrocyanicum dilutum U. S. P.). It is prepared by treating potassium cyanid with dilute sulfuric acid; thus:



This acid was first discovered by Scheele (1782), who prepared it from Prussian blue by distilling it with a mineral acid. He correspondingly called it "prussic acid," which, however, contains 4% of the anhydrous acid, and is, therefore, twice as strong as the official dilute acid. In cases of poisoning the best antidotes are mild inhalations of ammonia or chlorin, the application of cold water to the head and spine and the ingestion of the following solution in the order named: (1) Potassium carbonate, 20 grains in a fluid ounce of water; (2) ferrous sulfate, 10 grains in a fluidounce of water, and tincture ferric chlorid, 1 fluidram; the object of the above order being, first, to form potassium cyanid; second, the ferrocyanid and, third, the ferric ferrocyanid (insoluble). Upon standing HCN decomposes into ammonium formate: $\text{HCN} + 2\text{H}_2\text{O} = \text{HCOO} \cdot \text{NH}_4$.

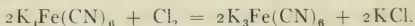
POTASSIUM FERROCYANID, yellow cyanid of potash, yellow prussiate of potash (potassii ferrocyanidum U. S. P.), $\text{K}_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$. This is prepared by heating potassium carbonate free from sulfate and introducing a mixture of iron filings and charcoal obtained from refuse matter rich in nitrogen (evaporated blood, horse hair, hoofs or horns). When the carbon dioxid and inflammable gases cease to be given off, the liquid mass is poured out, cooled and lixiviated with water. The resulting solution is crystallized, the crystals redissolved in water and repurified by recrystallization.

DESCRIPTION AND PROPERTIES.—The salt occurs in large, lemon-yellow, soft, translucent

crystals; odorless, with a sweet saline taste, neutral reaction and slightly efflorescent; soluble in four parts of water, insoluble in alcohol.

Tests.—Aqueous solutions of the salt with ferric chlorid give dark blue precipitates (Prussian blue); with ferrous salts, bluish-white precipitates are formed which gradually turn greenish-blue; with copper salts, chocolate-brown precipitates, and with lead acetate, white precipitates are formed. The salt should not effervesce with dilute sulfuric acid (carbonates); with hydrochloric acid and barium chlorid, only slight cloudiness (limit of sulfates). Fused with potassium nitrate and dissolved in water, filtered and the filtrate treated with silver nitrate, it should give but slight white precipitate (limit of chlorids).

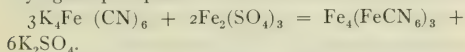
POTASSIUM FERRICYANID, red prussiate of potash, $K_3Fe(CN)_6$. This salt is made by the reduction of potassium ferrocyanid with chlorin; thus:



A solution is made of potassium ferrocyanid, the chlorin passed into the liquid changes its color from yellow to red. It is tested from time to time with ferric chlorid, and when it ceases to produce a blue color with it, it is concentrated by evaporation and crystallized. On exposure to air the salt decomposes into ferrocyanid. The salt is not official and is only valued as a test solution, producing with ferrous salts a dark blue precipitate (Turnbull's blue); with copper salts, a brownish-yellow precipitate; with silver

salts, orange precipitates; with mercurous salts, reddish-brown; but no precipitates are formed with either ferric, mercuric or plumbic salts.

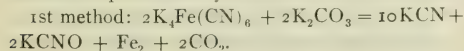
IRON FERROCYANID, Prussian blue, Williamson's blue, Paris blue, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$. This salt, while not official, is of technical interest. It is prepared by double decomposition between potassium ferrocyanid and a ferric salt, washing and drying the precipitate:



It is also made on a large scale by precipitating ferrous sulfate with potassium ferrocyanid and exposing the bluish precipitate to the air till it oxidizes and acquires color of proper depth.

POTASSIUM CYANID (potassii cyanidum U. S. P.). Two varieties of this salt are known in commerce—(1) the commercial cyanid, which is used for photographic purposes, and made by fusing dried potassium ferrocyanid with potassium carbonate, decanting the semiliquid mass from the sediment of iron and allowing it to cool and solidify. The potassium cyanate, which is a by-product in this reaction, is dissolved out with carbon disulfid.

The second method for the production of (2) pure potassium cyanid is by neutralizing hydrocyanic acid with potassium hydroxid. This is most conveniently done by passing HCN gas into an alcoholic solution of potassium hydroxid:



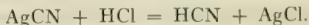
2d method: $\text{HCN} + \text{KOH} = \text{KCN} + \text{H}_2\text{O}$.

Potassium cyanid occurs in white, opaque, amorphous pieces or granular powder; odorless when dry, deliquescent in air, emitting the odor of HCN. It is soluble in 2 parts of water, sparingly in alcohol. It should be 90% pure; is strongly alkaline, usually containing 10% of a carbonate. It is used in the arts as a solvent in the manufacture of polishing agents; in the electroplating industries, also for the extraction of gold and silver from the rocks with which it forms soluble compounds. It is a strong poison.

SILVER CYANID (argenti cyanidum U. S. P.), AgCN , is prepared by precipitating silver nitrate with potassium cyanid; thus:

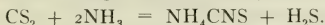


The salt should be 99.9% pure, which corresponds to 80.48% of metallic silver. It is a white, odorless and tasteless powder, permanent, but gradually turning brown, and should be preserved in the dark. It is insoluble in water, alcohol or cold nitric acid, but soluble in boiling nitric acid, evolving HCN. It is also soluble in ammonia water, potassium cyanid and sodium thiosulfate solution. The only use made of the salt is for the extemporaneous preparation of the official dilute hydrocyanic acid, which is done by mixing silver cyanid, 6 parts, with mixture of hydrochloric acid, 5, and water, 55 parts, agitating until all of the silver chlorid precipitates and pouring off the solution of HCN. The reaction is as follows:



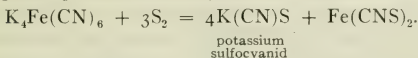
AMMONIUM SULFOCYANID, NH_4CNS , ammo-

mium thiocyanate, is made by dissolving carbon disulfid in alcohol and heating in the presence of ammonia, according to the following reaction:

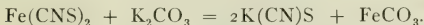


This salt is very analogous to the following:

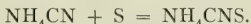
POTASSIUM SULFOCYANID, KCNS , potassium thiocyanate. This salt may be prepared by fusing together potassium ferrocyanid and sulfur:



The fused mass is next boiled with a solution of potassium carbonate which converts the ferrous sulfocyanid into potassium sulfocyanid and ferrous carbonate, which latter precipitates:



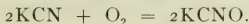
The soluble sulfocyanids can be prepared by direct union of the soluble cyanids with sulfur, as follows:



Potassium sulfocyanid is present in minute quantities in the human saliva.

Tests.—With ferric chlorid, the sulfocyanids give a blood-red coloration, which is not discharged by strong hydrochloric acid, thus distinguishing it from the red ferric acetate.

POTASSIUM CYANATE, KCNO . This may be prepared by exposing fused potassium carbonate for some time to the air; the salt absorbs oxygen from the air and is converted into the cyanate:

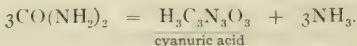


The salt can also be prepared by adding lead oxid to fused potassium cyanid; the potassium salt unites with the oxygen of the lead, forming the cyanate and setting the metal free.

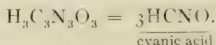
AMMONIUM CYANATE, NH_4CNO , a very soluble salt, which can be prepared by mixing a solution of potassium cyanate and ammonium sulfate. A double decomposition takes place, forming potassium sulfate in addition to the ammonium salt. This, upon the addition of alcohol, precipitates the potassium sulfate, leaving the ammonium cyanate in solution:



This salt is very interesting chemically, because it is isomeric with urea, $\text{CO}(\text{NH}_2)_2$. Urea can be prepared from ammonium cyanate by simply evaporating its solution to dryness on the water-bath. It is evident, therefore, that boiling water is sufficient to rearrange the atoms in the molecule; on the other hand, urea may be reconverted into ammonium cyanate by heating it to dull redness. When this is done, cyanuric acid forms and ammonia gas is given off:



If cyanuric acid is heated more strongly, it splits into cyanic acid, which distills over:



If, now, the cyanic acid be neutralized with the ammonia previously evolved, ammonium cyanate is reproduced.

Other organic compounds of nitrogen will be discussed in a special chapter.

THE ETHERS.

(R—O—R)

Name	Molecular formula	Boiling-point	Specific gravity
Dimethyl ether	C ₂ H ₆ O	23.6°	
Diethyl ether	C ₄ H ₁₀ O	34.6°	0.731 (4°)
Dipropyl ether.....	C ₆ H ₁₄ O	90.7°	0.763 (0°)
Di-isopropyl ether.....	C ₆ H ₁₄ O	69°	0.743 (0°)
Di-normal-butyl ether...	C ₈ H ₁₈ O	141°	0.784 (0°)
Di-secondary-butyl ether	C ₈ H ₁₈ O	121°	0.756 (21°)
Di-isobutyl ether.....	C ₈ H ₁₈ O	122°	0.762 (15°)
Di-isoamyl ether	C ₁₀ H ₂₂ O	170°	0.799 (0°)
Di-normal-octyl ether...	C ₁₆ H ₃₄ O	280°	0.805 (17°)
		Melting-point	
Dicetyl ether.....	C ₃₂ H ₆₆ O	55°	

As has been shown, alcohols correspond to the inorganic alkali hydroxids. Similarly, it may be stated that ethers correspond to metallic oxids.

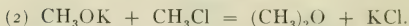
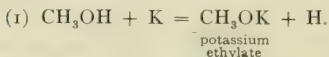
The ethers are formed by replacing the hydrogen of the hydroxyl of an alcohol with an alkyl. The compound ethers may be formed by a similar introduction of an acid radical or by replacing the hydrogen of the carboxyl of an acid with an alkyl. Mixed ethers, on the other hand, are oxids of two different alkyls; thus:

Simple ether is ethyl oxid, C₂H₅—O—C₂H₅.

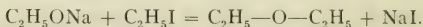
Compound ether (or ester) may be represented by ethyl acetate, CH₃COOC₂H₅.

Mixed ether may be represented by methyl-ethyl ether, $\text{CH}_3\text{OC}_2\text{H}_5$.

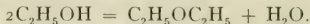
Preparation.—(1) *Simple ethers.* These may be prepared by treating an alcohol with an alkali metal and the resulting compound with their halogen derivative of a hydrocarbon. Thus, methyl ether may be prepared as follows:



Ethyl ether, "sulfuric ether," ethyl oxid, is the ordinary ether (æther U. S. P.). This is the common ether as we know it. It can be formed when sodium ethylete is warmed with ethyl halid. This is the "synthesis of Williamson," which not only indicates the formation of ether, but also its structure:



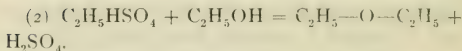
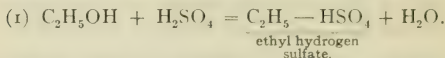
Ethyl ether is prepared on a large scale by heating alcohol with dehydrating agents, such as sulfuric acid; thus, if we abstract from two molecules of alcohol one molecule of water, ether results, according to the following equation:



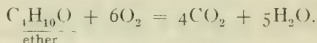
It can be prepared by heating a mixture of 5 parts of 90% alcohol and 9 parts of concentrated sulfuric acid in a flask provided with a thermometer and a dropping funnel and connected with a condenser. When the temperature rises to 140° , the mixture will

begin to boil and ether distills over. Alcohol is now slowly run in from the dropping funnel, the temperature at the same time being carefully regulated to $140-145^{\circ}$, until a considerable quantity of the ether passes over. The liquid in the receiver may be said to be a crude mixture of ether, alcohol and water, and in addition it contains sulfur dioxid which is produced by the decomposition of the acid. This is shaken with dilute soda in a separatory funnel, the layer of ether which floats on the surface is carefully separated and distilled from quicklime and purified by redistilling from a water-bath. The ether so prepared is about 90% pure and contains traces of alcohol and water. These are removed by adding pieces of bright metallic sodium, allowing to stand for several hours and again distilling. Sodium ethylate and hydroxid remain behind and pure ether passes over. The ether, in order to answer the requirements of the Pharmacopœia, must be at least 96% pure. The reaction described above is known as the "continuous ether process"; that is to say, with a given quantity of ether which serves there as a dehydrating agent only, unlimited quantities of ether should be prepared. As a matter of fact, a comparatively small quantity of the acid transforms a very large quantity of the alcohol, but the process has a limit in that the acid finally becomes diluted with the abstracted water and a part of it is reduced with the formation of sulfur dioxid. The reaction really takes place in two stages: first, the alcohol is converted into ethyl hydrogen sulfate (sulfovinic

acid), this compound next interacts with alcohol, yielding ether and sulfuric acid; thus:



Properties.—Ethyl ether, misnamed “sulfuric ether,” because sulfuric acid is used in its manufacture, is a colorless, very volatile and highly inflammable liquid, having a specific gravity of 0.726, a boiling-point of 35°, and containing not more than 4% of alcohol. With air it forms a highly explosive mixture:



Its vapor is heavier than air, and its administration by artificial light is only permissible when the source of the latter is high above the source of the ether. Under no circumstances should ether be evaporated over an open flame. It is soluble in about ten parts of water and in all proportions in alcohol and other organic solvents; it is also a good solvent, especially for all the organic acids (distinction from inorganic acids). It is employed in considerable quantities in surgery, principally because when inhaled it first produces intoxication and then anesthesia. In this respect it is similar to chloroform in that it causes insensibility. In pharmacy it is used as a solvent for resins, fats, oils, alkaloids, for the preparation of

collodions and the 32.5% spirit (spiritus ætheris U. S. P.); this, with 2.5% of ethereal oil, constitutes Hoffmann's anodyne (spiritus ætheris compositus U. S. P.)

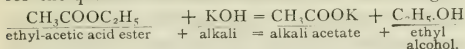
(2) *Mixed Ethers*.—**METHYL-ETHYL ETHER**, $\text{CH}_3\text{—O—C}_2\text{H}_5$, is prepared by distilling methyl alcohol with ethyl sulfuric acid. It is sometimes used as an anesthetic.

PROPERTIES OF THE ETHERS.—The ethers and esters of the lower members of the monatomic alcohols and of the fatty acids possess some general characteristics: they all have a pleasant odor, usually resembling that of some fruit, and mixtures of these have been used in the manufacture of synthetic fruit essences, or fruit ethers, sometimes called "fruit oils." Thus, artificial *pineapple* essence consists of chloroform, 1 part; aldehyd, 1 part; ethyl butyrate, 5 parts; amyl butyrate, 10 parts; with glycerin, 3 parts. *Strawberry* essence consists of ethyl nitrate, 1 part; ethyl acetate, 5 parts; ethyl formate, 1 part; ethyl butyrate 5 parts; methyl salicylate, 1 part; amyl acetate, 3 parts; amyl butyrate, 2 parts; with glycerin, 2 parts. *Pear* essence consists of ethyl acetate, 5 parts; amyl acetate, 10 parts; benzoic acid, 1 part; with glycerin, 10 parts. *Apple* essence is an alcoholic solution of amyl valerate. The ethers given under the first three headings above, and in the quantities given therein, should be dissolved in a sufficient quantity of pure alcohol to make 120 parts by measure. These mixtures are very powerful and very small quantities go a long way in producing the

flavors. When ingested in larger quantities they are deleterious. There are many other fruit essences or mixtures of ethers which are extensively employed to imitate whiskies, brandies, rums or wines, and some of them added in small quantities to young wines improve their "bouquet," which, ordinarily, is only produced in these by aging. On the other hand, the esters of the higher acids constitute the fixed oils and fats. All the esters of the monatomic alcohols and monobasic acids are neutral compounds, the lower members being volatile liquids, while the higher members are usually nonvolatile solids. The combinations with polyatomic alcohols and polybasic acids give rise to the neutral, acid or basic compound esters, closely analogous to the inorganic neutral, acid or basic salts. They sometimes give rise to compounds like glycerophosphoric acid, $C_3H_5(OH)_2H_2PO_4$, which in the same molecule affords the characteristics of all these varieties of compounds. The chief difference, chemically, between the ethers and the esters is in the fact that the ethers are not acted upon by alkali hydroxids, while the esters are decomposed, forming an alcohol and a salt of the alkali metal (soap).

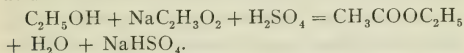
Saponification, as has been stated under Fats, is the term applied to a process resembling the action of alkali hydroxids upon the fats with the production of soap and glycerin. The same may be said that when an ester, such as ethyl acetate, is boiled with an alkali hydroxid, a salt (alkali acetate) and an alcohol (ethyl alcohol) are formed. This method is employed

not only for the identification of the esters, but also for the quantitative determination of their strength:



Among the esters of the aliphatic series, ethyl acetate, methyl salicylate, ethyl nitrite, ethyl sulfate, amyl nitrite and ethyl carbamate may be mentioned.

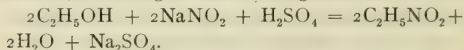
(3) *Esters*.—**ETHYL ACETATE**, acetic ether, acetic acid, ethyl-ester (æther aceticus U. S. P.), $\text{CH}_3\text{COOC}_2\text{H}_5$. It is prepared by distilling a mixture of sodium acetate and alcohol with sulfuric acid:



The distillate is washed with a solution of calcium chlorid, to free it from the water, then with milk of lime to free it from sulfuric acid. It is next decanted dried over calcium chlorid and finally redistilled. Acetic ether is an inflammable, colorless, limpid liquid, boiling at 76° , and having a specific gravity of 0.885. It possesses a pleasant, fruity odor, not unlike that of apples, hence it has gained the name of "apple oil." It is soluble in about 8 parts of water, which becomes slightly acid from its decomposition into acetic acid and alcohol (hydrolysis). It is soluble in alcohol and all the other organic solvents, and serves as a good solvent for the essential oils, resins, nitrocellulose and morphin. Small quantities of it added to hock wine and to eau de cologne improve their odor.

ETHYL NITRITE, nitrous ether, $\text{C}_2\text{H}_5\text{—O—NO}$,

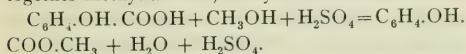
is a fragrant, ethereal mobile liquid, with a boiling-point of 16.5° and a specific gravity of 0.947. It is insoluble in water, but freely soluble in alcohol and other organic solvents. It is made by decomposing sodium nitrite with sulfuric acid in presence of ethyl alcohol, according to the following reaction:



This ether is official in the spirit of nitrous ether, sometimes called "sweet spirit of nitre"; spiritus ætheris dulcis (spiritus ætheris nitrosi U. S. P.). The spirit is an alcoholic solution containing about 4% of the ester; when assayed, this spirit should yield eleven times its own volume of nitric oxid (NO). The spirit is made by decomposing the sodium nitrite with the acid in presence of alcohol, as stated above, washing it with ice-water in which the potassium sulfate is but sparingly soluble, adding a solution of sodium carbonate to neutralize the sulfuric acid, separating the ether, drying it with potassium carbonate and filtering it into 22 times its own weight of alcohol. The spirit is used as a diaphoretic and diuretic. It is incompatible with many common chemicals and drugs, chief of which are antipyrin, sodium salicylate, potassium iodid, fluid extract of buchu and the tannates.

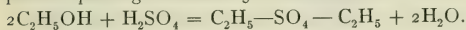
METHYL SALICYLATE, "artificial oil of winter-green," synthetic oil of wintergreen, $\text{C}_6\text{H}_4\text{—OH—COOCH}_3$. Methyl salicylate is a colorless liquid, possessing a strong odor and taste of the oil of gaultheria, which latter is composed almost entirely

of the above ester. It is also identical with the oil of sweet birch (*betula*). The liquid boils at 220° , and has a specific gravity of 1.183 to 1.185. It is slightly soluble in water, but freely soluble in alcohol and the organic solvents. It is made by heating together methyl alcohol, salicylic and sulfuric acids:



The ester is employed as a flavoring agent and as external application in rheumatism.

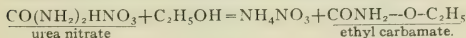
ETHYL SULFATE, heavy oil of wine, is the true sulfuric ether, $\text{C}_2\text{H}_5\text{—SO}_4\text{—C}_2\text{H}_5$. This is a heavy yellow oily liquid, prepared by mixing equal volumes of alcohol and sulfuric acid and, after twenty-four hours, subjecting to distillation and collecting the portion passing between 150 and 160°C .



When mixed with an equal volume of ether, it constitutes the official ethereal oil (*oleum æthereum* U. S. P.), a constituent of Hoffmann's anodyne.

ETHYL CARBAMATE, urethane, ethyl urethane, $\begin{array}{l} \diagup \text{NH}_2 \\ \text{CO} \\ \diagdown \text{OC}_2\text{H}_5 \end{array}$ (*æthylis carbamas* U. S. P.), an ester of

carbamic acid obtained by reacting with ethyl alcohol upon carbamid (urea) or one of its salts. It occurs in colorless, odorless prisms, melting between 50 and 51°C ., and soluble in 1 part water, 0.6 part alcohol and the other organic solvents. Reaction:



The salt is reputed as an excellent hypnotic, free from untoward after-effects.

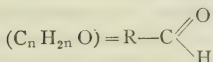
AMYL NITRITE (amylis nitris U. S. P.), $C_5H_{11}ONO$. It is a slightly yellowish liquid possessing the suffocating odor characteristic of the amyl compounds, a boiling-point of 96° and a specific gravity of 0.873. It is prepared by the action of nitrous acid on pentyl alcohol. The liquid is distilled and purified by washing and rectification. It is insoluble in water, but miscible with all of the organic solvents. It volatilizes at ordinary temperatures, and can best be kept in hermetically sealed glass bulbs or pearls which can be crushed in a handkerchief for inhalation. It is used as a heart tonic. The liquid should be composed of at least 80% of amyl nitrite, chiefly the iso-amyl, 0.26 grams of which, when assayed by the official process, should yield about 40 c.c. of gas.

SALACETOL, salantol, acetol salicylate, $C_6H_4(OH)CO-OCH_2-COCH_3$. It is prepared by the interaction between monochlor-acetone and sodium salicylate. The salt was introduced as a substitute for salol. It occurs in fine, needle-shaped crystals, melting at 71° ; insoluble in water and cold alcohol, but freely soluble in hot alcohol and the other organic solvents.

Other ethers of importance, such as ethyl and methyl benzoate, butyrate, valerate and nitrate, are all prepared by a process similar to the one given under Ethyl Acetate.

CHAPTER XXVII.

THE ALDEHYDS.

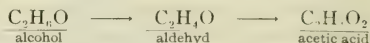


Name	Formula	Boiling-point
Formaldchyd.....	H.CHO	—
Acetaldehyd.....	CH ₃ .CHO	21°
Propionaldehyd.....	C ₂ H ₅ .CHO	49°
Butyraldehyd.....	C ₃ H ₇ .CHO	74°
Isobutyraldehyd.....	C ₃ H ₇ .CHO	63°
Valeraldehyd.....	C ₄ H ₉ .CHO	102°
Isovaleraldehyd.....	C ₄ H ₉ .CHO	92°
Capronaldehyd.....	C ₆ H ₁₁ .CHO	128°
Heptaldehyd or (Enanthol).....	C ₆ H ₁₁ .CHO	155°

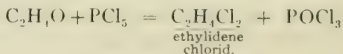
THE examination of the above list of aldehyds and the general formula for the same will show that they are alcohols minus two hydrogen atoms. The name aldehyd was derived from dehydrogenized alcohol (*alcohol dehydrogenatus*). They are obtained by the oxidation of the primary alcohols. The lowest member of the series is obtained by the oxidation of the lowest alcohol, namely, methyl alcohol. This aldehyd has sometimes been named methaldehyd, but at the present time the nomenclature of the aldehyds is obtained from the acids they form upon oxidation. Thus, the aldehyd of methyl alcohol, upon oxidation,

yields formic acid, and has, therefore, been named form-aldehyd. The aldehyd of ethyl alcohol upon oxidation yields acetic acid and has accordingly been named acet-aldehyd. The aldehyd of the third alcohol yields proprionic acid and, correspondingly, has been called proprion-aldehyd.

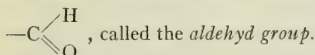
Preparation.—When the primary alcohols are mildly oxidized, two hydrogens are removed, splitting off water, and aldehyd is formed. By further oxidation, aldehyd takes up oxygen and becomes an acid. Aldehyds are, therefore, the intermediate products between the alcohols and acids; thus:



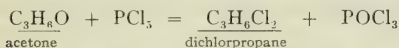
Properties.—The characteristic property of all aldehyds is their power to combine directly with ammonia, hydrocyanic acid, the alkaline sulfites and many other substances. They are strong reducing agents. Thus, when aldehyd is added to a solution of silver nitrate, rendered alkaline with ammonia water, the solution is reduced, and metallic silver is deposited on the walls, forming a mirror. By oxidation aldehyds are converted into acids, and by a process of reduction they are reconverted into alcohols. The structure of the aldehyds may be proven by the action of phosphorus pentachloride upon them, producing a dihalide derivative and splitting off phosphoric oxychloride, as follows:



It will be seen from the above that an atom of divalent oxygen was replaced by two monovalent chlorins, indicating the presence of the characteristic radical *carbonyl*, a carbon atom in combination with oxygen ($C=O$) and the absence of the hydroxyl ($-OH$) group. These peculiar properties of the aldehyds presuppose the presence of the group

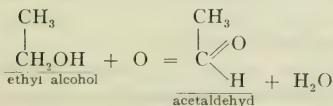
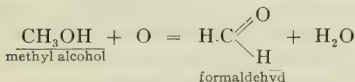


When ketones are treated similarly to aldehyds with phosphorus pentachlorid, a similar dihalid substitution product is formed, and phosphoric oxychlorid is split off; thus:

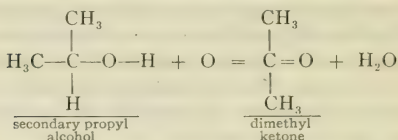


This reaction shows that the $=C=O$ group must exist in both classes of compounds and, indeed, this latter group is characteristic of all the ketones.

Whereas the aldehyds are produced from primary alcohols alone, the carbonyl (CO) group must be present at the end of a carbon chain; thus:



In the ketones, however, the carbonyl group must be located in the middle of a carbon chain; thus:



Furthermore, it may be stated that aldehyds can be oxidized without breaking the carbon chain, whereas the ketones when subjected to oxidation lose both carbon and hydrogen in the process. This can be illustrated by the oxidation of acetaldehyd, which produces acetic acid, and of dimethyl ketone which decomposes into acetic acid, carbon dioxid and water.

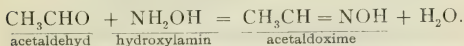
Aldehyds and ketones pass into alcohols on reduction. Thus, acetaldehyd forms ethyl alcohol, while acetone yields secondary propyl alcohol. With hydrocyanic acid an additive compound is formed, known as *cyanhydrin*, of the aldehyd or ketone employed. Thus, aldehyd gives acetaldehyd cyanhydrin, $\text{CH}_3\text{CH}(\text{OH})\text{CN}$, while acetone forms acetone cyanhydrin, $\text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$. With a saturated solution of sodium bisulfite, addition compounds known as *bisulfite compounds* of the respective aldehyd or ketone are formed; thus:



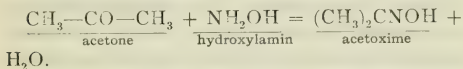
When the above compound is formed with acetal-

dehyd, it is known as *acetaldehyd sodium bisulfite*, or "ethyl-oxy-sulfonate of sodium."

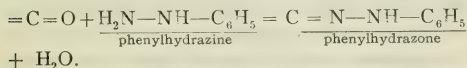
When aldehyds and ketones are reduced with hydroxylamin by the removal of oxygen, *oximes* are formed. Thus, when aldehyds are treated with hydroxylamin, *aldoximes* are formed:



With ketones a similar reaction occurs, giving rise to *keto oximes*, thus:



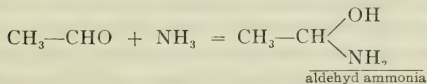
With hydrazin (NH_2-NH_2), phenylhydrazin ($\text{NH}-\text{C}_6\text{H}_5.\text{NH}_2$) and some other derivatives, aldehyds and ketones combine splitting off water, forming hydrazones and phenylhydrazones; thus:



In the case of acetaldehyd, the product is known as acetaldehyd-phenylhydrazone,

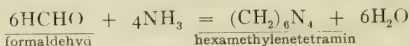


With ammonia, aldehyds form *aldehyd-ammonias*; thus:



The aldehyd ammonias are soluble in water, are decomposed by acids with the formation of the

ammonium salt of the acid and the regeneration of the aldehyds. The only aldehyd which behaves differently is formic aldehyd which gives, with ammonia, hexamethylenetetramin; thus:

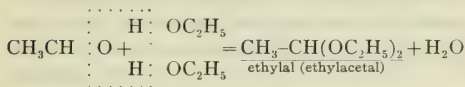


The above reaction is made use of in the determination of the strength of formaldehyd solutions. The caustic alkalis have different effects upon the aldehyds from ammonia. They resinify the lower members of the series, giving rise to a brown, resinous substance of unknown composition, called *aldehyd-resin*.

From the above comparison many points of similarity between the aldehyds and ketones can be seen. The points of difference between them are the following: (1) Aldehyds may be oxidized to monobasic acids containing the same number of carbon atoms, while the ketones (open chain), when oxidized, yield acids containing fewer carbon atoms, while the cyclic ketones form dibasic acids of the same number of carbons. (2) Aldehyds polymerize easily; ketones do not. (3) Aldehyds reduce ammoniacal solutions of silver nitrate; ketones do not. (4) Aldehyds redden solutions of magenta which have been decolorized by sulfur dioxide; ketones do not. (5) The aldehyds of the aromatic series are converted by caustic potash into a salt of the acid and an alcohol; ketones are not.

Aldehyds unite with the alcohols in the presence of

a little hydrochloric-acid gas, forming *acetals*. Thus, formaldehyd combines with methyl alcohol, giving *methythal*, $\text{H}_2\text{C}(\text{OCH}_3)_2$. Acetaldehyd with ethyl alcohol yields *acetal*, $\text{CH}_3\text{—CH}(\text{OC}_2\text{H}_5)_2$. The equation representing the reaction is as follows:



FORMALDEHYD, methaldehyd, formic aldehyd, “formalin,” HCHO , is obtained by the oxidation of methyl alcohol by bringing its vapor mixed with air in contact with heated platinum or copper. It may also be prepared by the dry distillation of calcium formate. Formaldehyd (Hofmann, 1867) is a very pungent, acrid gas which condenses to a liquid at -21° . The pure formaldehyd is very unstable. Its 40% water solutions are used extensively as antiseptics. The official solution (liquor formaldehydi U. S. P.) should contain not less than 37% by weight of absolute formaldehyd. The solution, when evaporated to the extent of 6 to 10 ounces to every 1000 cubic feet of room, according to Park, forms one of the most reliable disinfectants. The solution polymerizes very rapidly, forming paraformaldehyd, *paraform*. Paraform, chemically, is trioxymethylene, $(\text{CH}_2\text{O})_3$. It is prepared by slowly evaporating a solution of formaldehyd in methyl alcohol, when colorless crystals of paraform will separate. When heated, paraform splits into three molecules of

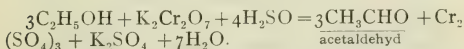
formaldehyd. It is a powerful agent employed for the preparation of formaldehyd, and its vapor has the advantage of not injuring the color of tapestries and fabrics of household goods. It is also used in bandaging.

The gas may be conveniently generated from an ordinary alcohol lamp filled with methyl alcohol and the projecting wick surrounded with some platinum foil. The lamp is lighted for a minute, then extinguished, when the platinum will continue to glow giving off formaldehyd. Formaldehyd is a strong antiseptic, and a few drops will preserve a considerable quantity of material. Thus, half a grain of formaldehyd will keep a quart of cow's milk sweet for several days. In technology formaldehyd has been employed for rendering gelatin and glue insoluble in water, also as a substitute for tannin in the leather industry. Lately it has been employed in the production of artificial silk by exposing fine threads of glue to the formaldehyd vapor. With the casein (pot-cheese) of cow's milk formaldehyd forms an insoluble substance which, when treated with talcum or heavy spar, is made into a stone-like material under the name of *gallalith*. Recently billiard-table balls and bowling-alley balls, as well as picture frames, have been made of gallalith.

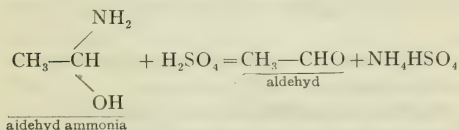
When a solution of formaldehyd is mixed with lime-water, it slowly polymerizes to a sweet syrup which, upon evaporation, gives a compound having the formula $(\text{CH}_2\text{O})_6$. This substance is known as *formose* and exhibits many properties indicating a close

relationship with grape-sugar. The above fact is very interesting, as it is supposed to have a bearing upon the production of sugar by plants. It is known that plants absorb carbon dioxid, and it is thought that during the assimilation of carbon dioxid by the green coloring matter (chlorophyl) in the presence of the sun's rays, it is converted, first, into formaldehyd which, by a process of polymerization, is converted into sugar.

ALDEHYD.—This name is commonly given to *acetaldehyd*, *ethaldehyd*, CH_3CHO . It is prepared by oxidation of ethyl alcohol with a solution of potassium dichromate in sulfuric acid:



It may also be produced by heating aldehyd ammonia with sulfuric acid; thus:

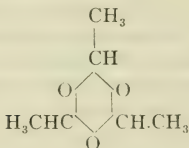


Aldehyd is a colorless, pungent liquid, readily soluble in water and boiling at 21°C . It polymerizes readily, giving rise to *paraldehyd*.

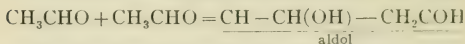
PARALDEHYD is a colorless liquid, boiling at 124°C . and having the formula $(\text{CH}_3\text{CHO})_3$. It is not an aldehyd, chemically, for it does not combine with either ammonia, sodium bisulfite, nor does it

reduce ammoniacal silver nitrate. It is prepared by adding a few drops of concentrated sulfuric acid to aldehyd. The liquid becomes hot, and when cooled to 0° C. solidifies, forming crystals of paraldehyd, which liquefy at 11° C. Paraldehyd (paraldehydum U. S. P.) is soluble in water, and is one of the official hypnotics.

The structure is as follows:



Acetaldehyd undergoes another polymerization in presence of potassium carbonate. It condenses to hydroxybutaldehyd, commonly known as *aldol*

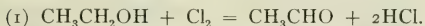


Aldol is a syrupy liquid, and the process is known as "aldol condensation."

TRICHLORALDEHYD, chloral, CCl_3CHO . Chloral is prepared by the prolonged action of chlorin upon absolute alcohol. It may be said, chemically, to be a substitution of acetaldehyd, although it cannot be obtained from it by the direct action of chlorin. The usual method of its production (Liebig, 1832), is by passing dry chlorin gas into alcohol. The reaction which takes place is a complicated one, giving several by-products. Of these,

the principal one is a compound of chloral and alcohol, known as *chloral-alcoholate*, and having the formula $\text{CCl}_3\text{—CH(OH)—OC}_2\text{H}_5$. This compound bears a relation to the acetals.

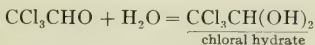
Preparation.—When a slow current of chlorin is passed through cooled ethyl alcohol, the latter is converted into aldehyd:



The liquid is next heated and the current of chlorin is continued until saturation. The chlorin acts upon the aldehyd, abstracting three-fourths of the hydrogen (united with the carbon), replacing it by chlorin, and thus producing chloral.

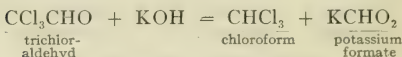
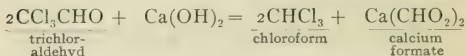


Description and Properties.—Chloral is an oily, heavy liquid with a pungent, irritating odor and a boiling-point of 98. It polymerizes like acetaldehyd on keeping or in the presence of small quantities of mineral acids. Upon addition of one-fifth of its bulk of water and shaking, the mixture solidifies with the evolution of considerable heat. The solid crystalline substance is known as *chloral hydrate* (chloral hydratum U. S. P.), or hydrated chloral, having the formula:

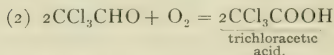
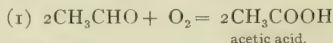


The hydrated chloral has a very faint odor of the liquid chloral attached to it. It is largely used in medicine as a hypnotic, and it has been stated that by the sodium carbonate of the blood it is decomposed

into chloroform, though this statement is doubted by some. Chloral hydrate is decomposed by caustic alkalis and alkalin carbonates into chloroform and a formate of the alkali metal. It is, therefore, incompatible with the alkalis and they should never be dispensed together.



Similarly to aldehyd, which, with nitric acid, is oxidized to acetic acid, chloral or trichloraldehyd is oxidized by nitric acid to trichloroacetic acid:



Trichloroacetic acid (acidum trichloroaceticum U. S. P.) is a monobasic, organic acid having the formula CCl_3COOH . It is obtained by oxidizing chloral hydrate with nitric acid. It occurs in white, deliquescent crystals with a characteristic odor, it should be preserved in amber glass and in a cool place. The acid is very soluble in all solvents, and when heated with alkali hydroxids, it decomposes into chloroform and alkali carbonate. Chloral, besides being decomposed by the alkali hydroxids and carbonates, is also affected by being triturated with

camphor, menthol, thymol, phenol and their derivatives, with which it liquefies. Chloral hydrate should with water, give a clear solution free from acid and chlorin.

BUTYL CHLORAL, $\text{CH}_3\text{—CHCl—CCl}_2\text{—CH(OH)}_2$, is obtained by passing chlorin into acetaldehyd, and has properties similar to chloral. A hydrate of this body, *butyl chloral hydrate*, erroneously called "croton chloral hydrate," has been used in medicine similarly to chloral. It corresponds in constitution with ordinary chloral in its being a butyl aldehyd— $\text{C}_3\text{H}_7\text{CHO}$ —from a molecule of which three hydrogens have been displaced by three chlorin atoms. *Bromal*, CBr_3CHO , is prepared like chloral, using bromin instead of chlorin. *Iodal* similarly prepared has the formula $\text{CI}_3\text{—CHO}$.

Besides butyl-chloral hydrate, the following compounds have been used as choral substitutes in medicine:

CHLORALAMID (chloralformamidum U. S. P.), a crystalline body made by direct union of formamid

$$\begin{array}{c} \text{OH} \\ \text{with choral, } \text{CCl}_3\text{CH} \begin{array}{l} \swarrow \\ \searrow \end{array} \begin{array}{l} \text{ } \\ \text{NH} \cdot \text{CHO} \end{array} \end{array}$$

. Melting-point,

115°; soluble in 20 parts water, 1.5 parts alcohol.

Chloralose, anhydroglucochloral (fr. glucose and chloral), $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_6$. Melting-point, 185°; soluble in 170 parts water, freely in alcohol.*

Hypnal, monochloral antipyrin (fr. antipyrin and chloral), a crystalline body soluble in 6 parts water.

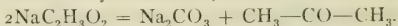
THE KETONES.



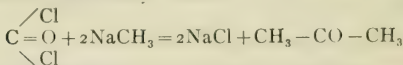
Name.	Formula.	Boiling-point.
Acetone or dimethyl ketone.....	$\text{CH}_3.\text{CO}.\text{CH}_3$	56.°
Propione or diethyl ketone.....	$\text{C}_2\text{H}_5.\text{CO}.\text{C}_2\text{H}_5$	103.°
Butyrone or dipropyl ketone.....	$\text{C}_3\text{H}_7.\text{CO}.\text{C}_3\text{H}_7$	144.°
Isobutyronone or di-isopropyl ketone	$\text{C}_3\text{H}_7\text{CO}.\text{C}_3\text{H}_7$	125.°
Isovalerone or di-isobutyl ketone	$\text{C}_4\text{H}_9\text{CO}.\text{C}_4\text{H}_9$	187.°
Caprone or diamyl ketone.....	$\text{C}_5\text{H}_{11}\text{CO}.\text{C}_5\text{H}_{11}$	227.°
		Melting point
Enanthone or dihexyl ketone....	$\text{C}_6\text{H}_{13}\text{CO}.\text{C}_6\text{H}_{13}$	305.°

As has been said before, ketones resemble aldehyds in some respects, but they contain the group =CO. The simplest of the ketones or acetones is the ordinary *dimethyl ketone*, $\text{CH}_3\text{—CO—CH}_3$, or acetone.

ACETONE is prepared by subjecting metallic acetates to dry distillation; thus:



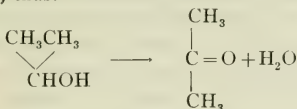
Another synthetical reaction which also demonstrates its structure is by the action of sodium methide on carbonyl chlorid:



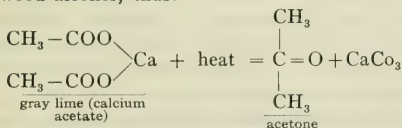
Under Aldehyds, we stated that all primary alcohols upon oxidation form first the corresponding aldehyds which pass into the fatty acids containing the same number of carbon atoms; thus:



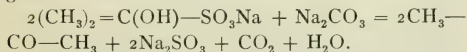
The secondary alcohols upon oxidation form ketones; thus:



Acetone is prepared on a commercial scale by subjecting to dry distillation the ordinary "gray lime" obtained as a by-product in the manufacture of wood alcohol; thus:



The so-obtained acetone may be purified by adding sodium bisulfite solution and converting it into the crystalline acetone sodium bisulfite which, when filtered, pressed and distilled with sodium carbonate, gives acetone:



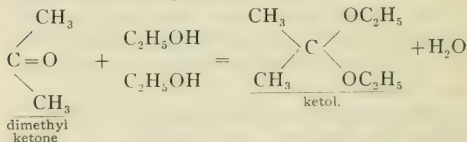
The acetone which passes over is dehydrated by calcium chlorid and redistilled.

Description and Properties.—Acetone (acetoneum U. S. P.) should contain not less than 99% by weight of absolute dimethyl ketone. It is a colorless liquid, with a fragrant odor similar to methyl alcohol; soluble in water, and having a boiling-point of 56° and a specific gravity of 0.792 (20°). It is soluble in water, alcohol and other organic solvents. It is

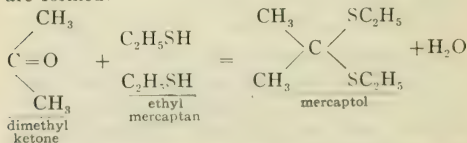
sometimes contained in the breath of diabetic patients and in the urine—in which it may be detected by the iodoform reaction (Lieben's test). It is employed chiefly as a solvent for nitrocellulose, with which it forms collodions known as "acetone collodions." It is also used as a solvent in the preparation of the official oleoresins, and in the manufacture of iodoform, chloroform, sulfonal, etc.

When acetone, mixed with twice its weight of 70% sulfuric acid, is subjected to distillation, *mesitylene* passes over. Mesitylene is, chemically, trimethyl benzene, C_9H_{12} , and may be said to be a condensation product of three molecules of acetone from which three molecules of water have been removed.

KETOLS AND MERCAPTOLS.—When ketones unite with alcohols, *ketols* are formed:

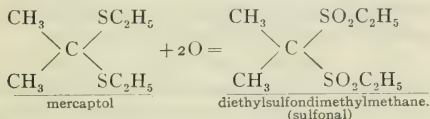


When ketones unite with mercaptans, *mercaptols* are formed:



When mercaptols are oxidized, they take up oxygen much like the mercaptans, forming com-

pounds containing sulfonic acid. Thus, when mercaptol is treated with two molecules of oxygen, diethylsulfondimethylmethane, or sulfonal, is formed, according to the following reaction:



SULFONAL is a colorless, tasteless, inodorous, crystalline body, with a melting-point of $125-126^\circ \text{C}$. and a boiling-point of 300°C . It is soluble in 15 parts of boiling water, 500 parts of cold water and in 65 parts of alcohol. It is used as a hypnotic. It is official under the title *sulphonmethane* (sulphonmethanum U. S. P.).

When one methyl group of sulfonal is replaced by an ethyl group, $\begin{array}{c} \text{CH}_3 \quad \text{SO}_2\text{C}_2\text{H}_5 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C}_2\text{H}_5 \quad \text{SO}_2\text{C}_2\text{H}_5 \end{array}$ **TRIONAL** is formed.

It is prepared by the oxidation of a mercaptol with ethylmercaptan. It is official as sulfonethylmethane (sulphonethylmethanum U. S. P.). Trional forms colorless, shining crystals, melting at 76°C ., and soluble in 320 parts cold water; freely soluble in hot water, alcohol and other organic solvents.

When both methyl radicals of sulfonal are replaced by ethyl radicals, $\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{SO}_2\text{C}_2\text{H}_5 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C}_2\text{H}_5 \quad \text{SO}_2\text{C}_2\text{H}_5 \end{array}$ diethylsulfon-

diethylmethane (**TETRONAL**) is produced. The method of preparation of tetronal differs from that of sulfonal in that diethyl ketone is employed in the place of acetone. It occurs in crystalline scales, melting at 89° C., soluble in 450 parts cold water, readily in alcohol and other organic solvents.

There seems to be some connection between the hypnotic action of sulfonal and the ethyl radicals it contains, for, while dimethylsulfondimethylmethane does not produce sleep, dimethylsulfondiethylmethane does. Hence the supposition that trional with three, and tetronal with four ethyl radicals should act as stronger and safer hypnotics than sulfonal, and by experience, the supposition has been confirmed.

CHAPTER XXVIII.
THE FATTY ACIDS.
($C_nH_{2n}O_2$ or $C_nH_{2n-1}COOH$)

Name	Empiric formula		Chemical formula	Melting-point	Boiling-point	Specific gravity
Formic.....	CH_2O_2		$H.CO.OH$	8.3°	101°	1.231(10°)
Acetic.....	$C_2H_4O_2$		$CH_3.CO.OH$	16.5°	118°	1.052(16.5°)
Propionic	$C_3H_6O_2$		$C_2H_5.CO.OH$	-24°	141°	1.013(0°)
Butyric	$C_4H_8O_2$		$C_3H_7.CO.OH$	-9° to +2°	162°	0.987(0°)
isobutyric	$C_4H_8O_2$		$(CH_3)_2CH.CO.OH$	—	154°	0.965(0°)
Valeric	$C_5H_{10}O_2$		$C_4H_9.CO.OH$	—	185°	0.956(0°)
Isovaleric	$C_5H_{10}O_2$		$(CH_3)_2CH.CH_2.CO.OH$	—	174°	0.947(0°)
Methylethylacetic	$C_5H_{10}O_2$		$(CH_3)(C_2H_5).CH.CO.OH$	—	177°	0.941(0°)
Trimethylacetic.....	$C_5H_{10}O_2$		$(CH_3)_3C.CO.OH$	35.4°	164°	0.905(50°)
Caproic (isobutyl acetic)...	$C_6H_{12}O_2$		$(CH_3)_2CH.CH_2.CO.OH$	-1.5°	200°	0.945(0°)
Enanthylic (heptylic)	$C_7H_{14}O_2$		$C_6H_{13}.CO.OH$	-10.5°	223°	0.931(0°)
Caprylic.....	$C_8H_{16}O_2$		$C_7H_{15}.CO.OH$	16.5°	236°	0.927(0°)
Pelargonic	$C_9H_{18}O_2$		$C_8H_{17}.CO.OH$	12.5°	186°	0.911(12°)
Capric.....	$C_{10}H_{20}O_2$		$C_9H_{19}.CO.OH$	31.4°	268°	0.930(27°)
Undecylic	$C_{11}H_{22}O_2$		$C_{10}H_{21}.CO.OH$	28°	275°-280°	—
Lauric.....	$C_{12}H_{24}O_2$		$C_{11}H_{23}.CO.OH$	44°	225°	0.875
Tridecylic.....	$C_{13}H_{26}O_2$		$C_{12}H_{25}.CO.OH$	40.5°	236°	—
Myristic.....	$C_{14}H_{28}O_2$		$C_{13}H_{27}.CO.OH$	54°	250°	0.862

At 100 mm pressure
At the boiling-pt.

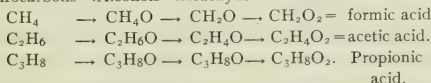
THE FATTY ACIDS.—Continued.

($C_nH_{2n}O_2$ or $C_nH_{2n}.COOH$)

Name	Empiric formula	Melting-point	Boiling-point	Specific gravity
Isocetic.....	$C_{15}H_{30}O_2$	55°	257°	—
Palmitic.....	$C_{16}H_{32}O_2$	62°	271°	0.852
Daturic.....	$C_{17}H_{34}O_2$	60°	277°	—
Stearic.....	$C_{18}H_{36}O_2$	71°	291°	0.845
Arachidic.....	$C_{20}H_{40}O_2$	75°	—	—
Behenic.....	$C_{22}H_{44}O_2$	77°	—	—
Lignoceric.....	$C_{24}H_{48}O_2$	80°	—	—
Carnaubic.....	$C_{24}H_{48}O_2$	72°	—	—
Hyenic.....	$C_{25}H_{50}O_2$	77°	—	—
Cerotic.....	$C_{27}H_{54}O_2$	78°	—	—
Melissic.....	$C_{30}H_{60}O_2$	90°	—	—
	$C_{14}H_{29}.CO.OH$		At 100 mm. pressure	At the melting-point
	$C_{15}H_{31}.CO.OH$			
	$C_{16}H_{33}.CO.OH$			
	$C_{17}H_{35}.CO.OH$			
	$C_{19}H_{39}.CO.OH$			
	Unknown ..			

When methyl, ethyl or propyl alcohols, all of which are monatomic, are subjected to oxidation, they are converted first into aldehyds, which take up oxygen and are converted into acids. The relationship is shown in the following table:

Hydrocarbons→Alcohols→Aldehyds→ Acids



All the above acids contain but two oxygen atoms in the molecule or one COOH (*carboxyl*) group, and are spoken of as monobasic acids.

When diatomic alcohols, are subjected to oxidation, acids having four oxygen atoms in the molecule or two carboxyl groups are formed, and are spoken of as dibasic acids. Similarly, we have tribasic acids and, if in addition to the carboxyl groups they contain also one or more—OH (hydroxyl) groups, they are spoken of as atomic acids; thus, tartaric acid has two hydroxyl groups and two carboxyl groups and is, therefore, spoken of as dibasic and diatomic. All organic acids contain at least one carboxyl radical or group. The carboxyl radical is sometimes known as *oxatyl*,—COOH, and is monovalent. The simplest organic acid in which the carboxyl is united to hydrogen is formic acid, H—COOH, and the series of acids of which it is the first and simplest member are sometimes called *formic acid* or the *fatty acid-series*.

The basisity of an organic acid depends upon

the number of carboxyl groups contained in the molecule. Thus, formic acid contains one carboxyl group and is, therefore, monobasic; oxalic acid contains two carboxyl groups and is, therefore,



dibasic | ; and citric acid, containing three



carboxyl and one hydroxyl group, is called a tribasic, monatomic acid. Acids containing the hydroxyl group in addition to the carboxyl are also spoken of as *oxy-* or *hydroxy acids*.

In this discussion no attempt will be made to cover all the acids, but only those of pharmaceutical importance will be taken up.

Properties.—The organic acids are feebler than the inorganic acids, but otherwise possess the same general properties. The higher and more complex acids are very weak in their acidic properties. A salt of an organic acid and a non-volatile metal, and upon incineration, is converted into the metallic carbonate. There are several homologous series of these organic acids, but the most important is the *fatty-acid series*, which derives its name from the fact that some of its higher members are found as salts of the glyceryl radical in fats. Many of the acids of this series, are found in nature; thus formic acid, which is the first member of the series, is found in stinging nettle and red ants. The second acid of the series is acetic acid, which occurs in many plants, in certain animal secretions, and can be readily distilled from vinegar. Butyric acid, the fourth member of the series, is found

in rancid butter, and valeric acid, the fifth member, is found in valerian root, etc.

Occurrence.—Besides the above sources, the higher acids are found in the animal fats, in the fats of plants, and free and combined as metallic and ethereal salts.

Varieties.—Above we have mentioned the *simple* and the *hydroxy acids*. Besides these we have *chlor-acids* which are formed when the hydrogen of an acid radical is replaced by chlorine. When the hydrogen of the acid radical is replaced by NH_2 , *amido acids* are obtained; when one of the oxygens of the carboxyl group is replaced by sulfur, *thio-acids* are produced.

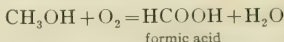
Preparation.—Several methods of preparation are known: (1) By decomposing metallic salts with sulfuric or hydrochloric acids; (2) by saponification of the esters; (3) by fermentation; (4) by destructive distillation; (5) by oxidation of the corresponding alcohols; (6) by hydrolysis of the hydrocarbon cyanids with alcoholic potash.

Characteristics of the Series.—The fatty acids form a homologous series, of which the first nine members are colorless liquids, showing a rise of about 22° in their boiling-points for each CH_2 group added; thus, butyric acid boils at 163.2° ; valeric acid, 184.5° .

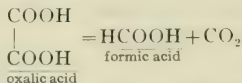
Beginning with pelargonic acid, $\text{C}_9\text{H}_{19}\text{COOH}$, which is a solid, all the higher members are also solids.

FORMIC ACID, $\text{H}-\text{COOH}$ or HCHO_2 , can be prepared by the oxidation of methyl alcohol either

by dropping it on spongy platinum or by distilling methyl alcohol with potassium dichromate and sulfuric acid. This latter mixture in presence of alcohol evolves oxygen with formation of potassium and chromium sulfates:

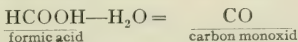


Formic acid can also be prepared by heating glycerol, with oxalic acid to about 100°C. , when formic acid will form and distill over with the water, while another portion of it combines with the glycerol, forming glyceryl monoformate. This second portion can be recovered and a second quantity of formic acid obtained by the addition of more crystallized oxalic acid and continued heating. The glycerol takes no part in the production of the formic acid, but modifies the method of decomposition of oxalic acid:



Properties.—Formic acid is a clear, colorless liquid with a pungent, penetrating odor, boiling at 101°C. , and having a specific gravity of 1.231 (10°). In the concentrated form it produces a blister when applied to the skin. All its salts are soluble in water, and these as well as the acid are decomposed by strong sulfuric acid with effervescence, yielding carbon monoxid. Pure carbon monoxid may readily be obtained by heating the acid with

strong sulfuric acid, the latter acting as a dehydrating agent:



Formic acid and its salts are strong reducing agents. On warming a few drops of it with an ammoniacal solution of silver nitrate, a silver, mirror-like deposit will form. This reaction distinguishes formic acid from all the other fatty acids, and is due

to the presence of the aldehyd group: $\text{HO}-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$.

The above is the principal test for the acid and the formates.

ACETIC ACID, CH_3COOH , is official in the Pharmacopœia in three forms: *acidum aceticum*, containing 36%; the dilute (*dilutum*), 6%, and the glacial (*glaciale*), 99%, respectively, of the absolute acid.

Acetic acid may be obtained by one of two principal methods: First, by the oxidation of alcohol; second, by the dry or destructive distillation of wood. By the first method we obtain vinegar; by the second, crude acetic, or *pyroligneous acid*.

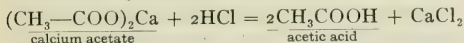
Vinegar.—When weak alcoholic solutions, such as wine, beer or cider, are exposed to the air, the vinegar organism (*mycoderma aceti*), also known as “mother vinegar” or acetous ferment, starts the fermentation. Strong alcoholic liquids—*i.e.*, those containing more than 15% of alcohol—prevent the activity of the organism. The 10% alcoholic solutions are the most favorable. The organism acts as a

carrier or "fixer" of oxygen between the air and the alcohol. Thus, we produce, by employing beer, *malt* vinegar; by employing wine, *wine* vinegar, containing 6% and 8% of acetic acid, respectively. Wine vinegar owes its aroma to ethyl acetate and propionate and other substances present in the wine.

Quick Vinegar Process.—In this "oxidation method" a dilute alcoholic solution, not over 10% strong, is permitted to slowly drop into a large cask perforated with holes for free admission of air and filled with clean wood shavings. Some warm, fermented malt liquor, such as beer, is poured upon the shavings and acts as the "mother of vinegar," or as the ferment. The alcoholic solution dripping through the cask when it comes in contact with the shavings coated with the ferment organisms, becomes oxidized, the temperature of the cask interior rises, causing a free circulation of air, and the alcoholic solution is rapidly converted into an impure solution of acetic acid which issues from an orifice at the bottom of the cask. By distilling vinegar we can obtain the free acetic acid.

Second Method.—As stated under the destructive distillation of wood, the aqueous solution produced therein, known as pyroligneous acid (containing acetic acid, methyl alcohol and acetone), is permitted to run into milk of lime, forming crude calcium acetate. When crude lime acetate is subjected to distillation, methyl alcohol and acetone are distilled off. The dry acetate is next distilled in copper

vessels with sufficient quantity of strong hydrochloric acid to decompose it:



The distillate contains about 50% of acetic acid, which is further purified by distillation over a little potassium dichromate. *Glacial acetic acid* is made by neutralizing the ordinary strong acetic acid with soda. This forms a compound crystallizing with three molecules of water and having the formula $\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}$. When fused, water of crystallization is expelled, and, upon addition of concentrated sulfuric acid and distillation, the salt is decomposed and pure acetic acid passes over. The pure acid solidifies on cooling, forming a crystalline mass resembling ice, from which its name “glacial” has originated. It melts at 16.7° and boils at 119° , and has a specific gravity of 1.049.

Properties, Uses and Tests.—Acetic acid is a useful solvent for organic substances because it is little affected by oxidizing agents. When it is mixed with water, contraction in volume takes place so that an aqueous solution frequently has a higher specific gravity than the pure acid, and for this reason the strength of acetic acid cannot safely be determined by hydrometer. It can be detected by its odor or by neutralizing the liquid with soda and evaporating to dryness. If sulfuric acid is now added to the residue, strong odor of vinegar develops, and, in the presence of a little alcohol, the fragrant odor of ethyl acetate will develop. With ferric chlorid,

acetic acid and the neutral acetates will give a deep red coloration, which is destroyed on boiling, forming an insoluble basic salt. Formic acid gives similar reactions, but it can be distinguished from acetic by its reducing power on silver nitrate solutions—a property not possessed by acetic acid. With silver nitrate, aqueous solutions of acetates give a characteristic crystalline precipitate of silver acetate which, when dried and ignited, leaves a residue equal to 64.6% of metallic silver. By this means a quantitative determination of the most satisfactory kind is made and also serves as a method for identifying organic acids. Many salts of acetic acid are official, of which the most common is lead acetate, “sugar of lead,” $\text{Pb}(\text{CH}_3\text{COO})_{2,3}\text{H}_2\text{O}$. This is obtained by dissolving lead carbonate in acetic acid, evaporating and crystallizing. A solution of the normal salt dissolves lead oxid (litharge) and forms basic acetate of lead (subacetate), $\text{Pb}_2\text{O}(\text{CH}_3\text{COO})_2$. This is the chief ingredient of Goulard’s extract (liquor plumbi subacetatis U. S. P.). This solution exposed to the air turns milky through the absorption of CO_2 gas. All soluble compounds of lead are poisonous, and magnesium or sodium sulfates serve as reliable antidotes, because they form with it insoluble lead sulfate. “Iron liquor” is a solution of the acetate of iron, and “red liquor” is a solution of aluminum acetate, both used as mordants in calico dyeing and printing.

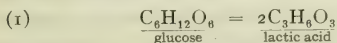
The calcium salt of acetic acid is used in the manufacture of acetone.

PROPIONIC ACID, $\text{CH}_3\text{CH}_2\text{COOH}$, is most

readily obtained by oxidizing propyl alcohol with a "pyrochromic mixture." (Pyrochromic mixture is a solution of potassium dichromate in concentrated sulfuric acid, and is the most commonly used oxidizing agent of organic chemistry.) Propionic acid is found among the products of certain fermentative processes. It is soluble in water, but is thrown out of its solution when calcium chlorid is added. Otherwise, it resembles acetic acid in odor and appearance and its properties, but has a boiling-point of 141°C . It may be synthetized by hydrolyzing ethyl cyanid ($\text{C}_2\text{H}_5\text{CN}$):



BUTYRIC ACID, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—COOH}$, occurs in two isomeric modifications: *Normal or fermentation butyric acid* (Chevreul, 1814), first found in butter, in which it is present to the extent of about 7% as a glyceryl ester. It is also found in the free state in perspiration and in certain animal secretions. The principal source of it is the fermentation known as "butyric." By mixing a solution of starch with putrid cheese and chalk in presence of tartaric acid and ammonium phosphate at a temperature of about 35°C ., butyric acid is formed. It may be said that the fermentation takes place in several stages; thus, the starch is first converted into glucose, this into lactic acid, and lactic acid into butyric acid:

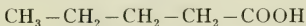


Among the products of this fermentation besides the butyric acid, acetic and caproic acids may be mentioned. The free butyric acid produced combines with the calcium, forming calcium butyrate, which is decomposed by hydrochloric acid, and butyric acid is separated by distillation. It may also be obtained by oxidizing normal butyl alcohol. Butyric acid is an oily liquid, possessing an unpleasant odor of perspiration and rancid butter. It is soluble in water but, like propionic acid, it is thrown out of solution by calcium chlorid. Its ester (ethyl butyrate) is employed in making artificial flavoring essence of peach. *Isobutyric acid* has been found free or as an ester in many plants.

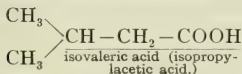
It has the formula $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array} \text{CH} - \text{COOH}$. It is found in the oil of chamomile, or may be prepared by oxidizing isobutyl alcohol or by the hydrolysis of isobutyronitril (isopropylcyanid). In appearance it closely resembles the normal acid, but is less soluble in water, and its calcium salt is more soluble in hot than in cold water.

VALERIC ACIDS.—"Valerianic" acid has the formula $\text{C}_5\text{H}_{10}\text{O}_2$ and exists in four isomeric modifications. Two of the isomerids, the isovaleric and methyl-ethyl acetic acids, are obtained by the oxidation of fusel oil. Isovaleric acid occurs as a glycerid in certain blubber oils. The above two acids are found together in the valerian group and in angelica, from which they may be obtained by distilling with water. They are oily liquids, slightly soluble in

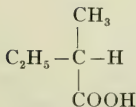
water. One of these, however, the methyl-ethyl acetic acid, exists in two modifications which cannot be distinguished in appearance or by chemical properties, but which differ in certain physical properties, namely, it is "optically active"—that is, it affects the plane of polarized light. All bodies possessing this property are known as "optically active" and must contain at least one *asymmetric carbon atom*. An asymmetric carbon atom is one in which each of the four bonds is united to a different atom or group. The following are the structural formulas of the four valeric acids, the third one of which is optically active because it contains one asymmetric carbon atom:



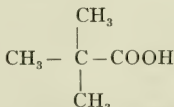
normal valeric acid (propylacetic acid)



isovaleric acid (isopropylacetic acid.)



active valeric acid (methyl-ethyl acetic acid)



trimethylacetic acid.

Commercially, isovaleric acid is obtained by the oxidation of the commercial amyl alcohol with pyrochromic mixture, and this is the source of the valerates employed in medicine. Valeric acid has an unpleasant, rancid odor, a boiling-point of 170° C. and a specific gravity of 0.941 (at 0° C.).

The higher homologues of the paraffinic acids occur frequently in the fats and oils and have been described under Fats.

LAURIC ACID, $C_{11}H_{23}COOH$, occurs in the seeds of the laurel—*Laurus nobilis*—and in the wood of the South American *Goupia tomentosa*.

MYRISTIC ACID, $C_{13}H_{27}COOH$, is found in the seeds of the wild nutmeg—*Myristica moschata*.

MARGARIC ACID, $C_{18}H_{33}COOH$, does not seem to occur in the common fats, but it can be prepared synthetically.

ARACHIDIC ACID, $C_{19}H_{39}COOH$, occurs in the African earth nut—*Arachis hypogea*.

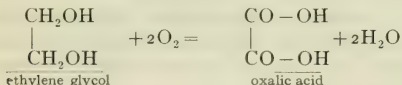
THE DIBASIC ACIDS.



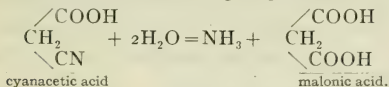
		Melting-point
Carbonic acid.....	HO.CO.OH
Oxalic acid.....	COOH.COOH	189°
Malonic acid.....	COOH.CH ₂ .COOH	134°
Succinic acid.....	COOH.CH ₂ .CH ₂ .COOH	182°
Glutaric acid.....	COOH.(CH ₂) ₃ .COOH	97°
Adipic acid.....	COOH.(CH ₂) ₄ .COOH	150°
Pimelic acid.....	COOH.(CH ₂) ₅ .COOH	103°

Preparation of the Dibasic Acids.—The dibasic acids are prepared by a process resembling the formation of the fatty acid series. The glycols, which name is applied to the diatomic alcohols, and which possess two primary alcohol groups, yield, on oxidation, dibasic acids. The simplest of the

dibasic acids and corresponding to the first glycol is *oxalic acid*:



It will be seen from the above that two oxygen atoms have been substituted for each two hydrogen atoms of the hydrocarbons. They contain two hydrogen atoms replaceable by metals or basic radicals. They can also be formed by hydrolysis of the cyanogen derivatives of the monobasic acids. Thus, cyanacetic acid will hydrolyze with water, splitting off ammonia and giving malonic acid:



They can also be produced by treating dicyanids ($\text{R}''(\text{CN})_2$) with caustic alkalis, and by oxidation of diatomic primary alcohols and the oxidation of hydroxyacids.

Besides these methods they may be obtained by electrolysis.

CARBONIC ACID, $\text{HO}-\text{COOH}$. While this acid has only one carboxyl group, its compounds, however, are those of a dibasic acid. Its metallic salts are fully described in the inorganic part of this book.

CARBONYL CHLORID, carbonoxychlorid, phos-

gene, $\text{CO} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array}$, is obtained by the direct union of

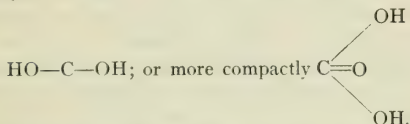
carbon monoxid and chlorin in sunlight (Davy, 1811). Carbonyl is also formed when chloroform is oxidized in the presence of air and light. On a large scale it is produced by passing a mixture of carbon monoxid and chlorin through heated charcoal. Carbonyl chlorid condenses to a liquid at 8° , and has a suffocating, pungent smell. It has been used for the manufacture of aniline dyes and specially of crystal violet.

UREA, carbamid, $\text{CO}(\text{NH}_2)_2$. This important amid is a normal constituent of urine and constitutes the chief form in which the waste nitrogen of the system is eliminated. It may be said to be derived from two molecules of ammonia in which two hydrogen atoms were replaced by the divalent carbonyl group. Its constitutional formula is the following:



It may be prepared by evaporating urine and adding to it strong nitric acid when, on standing, yellow crystals of urea nitrate will be deposited. These are collected on a filter, dissolved in boiling water and decomposed by barium carbonate, which forms barium nitrate and frees the urea. This is then evaporated to dryness on a water-bath and the dry residue is extracted with boiling alcohol, the solution is filtered and, when concentrated, deposits crystals of urea. It may also be produced from ammonium cyanate and carbonyl chlorid, both of which methods have already been described.

Derivatives of Carbonic Acid.—Carbonic acid is spoken of as methane, CH_4 , in which two hydrogens were replaced by two hydroxyl groups and the other two hydrogens by one oxygen. Its graphic formula may be written:



According to the above structure, sodium acid

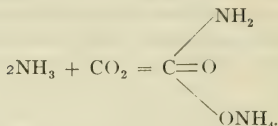
carbonate would be written, $\begin{array}{c} \text{OH} \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{O}-\text{Na} \end{array}$, the nor-

mal sodium carbonate, $\begin{array}{c} \text{O}-\text{Na} \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{O}-\text{Na} \end{array}$, and ammon-

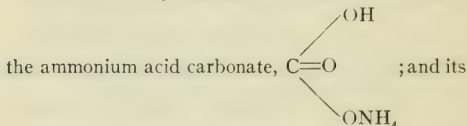
ium carbonate, $\begin{array}{c} \text{O}-\text{NH}_4 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{O}-\text{NH}_4 \end{array}$.

Allied to carbonic acid is *carbamic acid*; although it has never been isolated, its ammonium salt is a constituent of the official ammonium carbonate (ammonii carbonas). Thus ammonium carbamate,

$\text{NH}_4\text{COO.NH}_2$, is readily obtained by passing CO_2 into an alcoholic solution of ammonia gas:

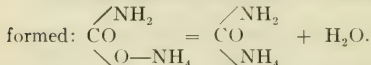


The Pharmacopoeial salt is a mixture of this and



formula is: $\text{NH}_4\text{HCO}_3.\text{NH}_4\text{NH}_2\text{CO}_2$.
 Official ammonium carbonate

When ammonium carbamate is heated, *urea* is



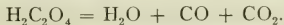
Urea may, therefore, be regarded as the amid of carbonic acid; that is, carbonic acid in which both the hydroxyl groups have been replaced by amid,— NH_2 , groups. It is often called *carbamid*.

Urea is found in the urine of mammals; thus, the normal daily quantity excreted by men is from 40 to 50 grams and by women 25 to 40 grams. Urea is the end-product of the proteid metabolism in the body, and represents about 85% of total nitrogen eliminated by the body; the quantity found in urine serves as a measure of the nitrogenous metabolism in the human body.

OXALIC ACID, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is a dibasic acid; it occurs in the form of fine crystals containing 2 molecules of water of crystallization. Oxalic acid may be prepared in several ways: (1) By oxidation of sugars, starches, etc., with nitric acid; (2) on the commercial scale, by heating saw-dust with caustic soda to 250°C . Sodium oxalate is produced by this method, which extracted, with lime water, is decomposed by strong sulfuric acid into insoluble calcium sulfate, the solution containing oxalic acid is decanted, filtered, evaporated to a small bulk and crystallized. Oxalic acid is a strong poison; it occurs naturally in juices of many plants, like sorrel, rhubarb, oak, cinchona, etc. It has been used for suicidal purposes; as antidotes, magnesia (MgO), slaked lime in a little water, or mucilaginous liquids should be given *at once*. If there is no vomiting, an emetic is administered. *Neither a stomach pump nor alkalis, or their carbonates* should be used.

Tests.—With calcium chlorid neutralized with ammonia water, the soluble oxalates give a crystalline precipitate soluble in hydrochloric, but insoluble in acetic acids.

Properties.—Oxalic acid is one of the very strongest organic acids, it is soluble in water; at 100°C . it loses its water of crystallization; it sublimes at 155°C .; when treated with strong sulfuric acid, it decomposes into water and the two carbon oxids:



Oxalic acid is a strong reducing agent, it decolorizes solutions of permanganates, and precipitates

gold and silver. It forms two classes of salts—acid and normal.

Acid potassium oxalate, “salts of sorrel,” binoxalate of potassium, occurs in sorrel, is used in eradicating iron and ink stains from fabrics, in manicuring,

etc.; it has the formula
$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOK.} \end{array}$$

Calcium oxalate is found in many plants, also as a crystalline deposit in urine; it has the formula—

$$\begin{array}{c} \text{COO} \\ | \\ \text{COO} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{Ca.}$$

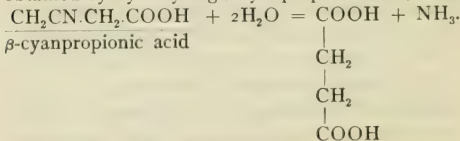
Sodium oxalate is
$$\begin{array}{c} \text{COONa} \\ | \\ \text{COONa} \end{array}, \text{ a normal salt.}$$

All ammonium, potassium and sodium oxalates are soluble; the oxalates of the other metals are practically insoluble.

MALONIC ACID is a very valuable reagent in organic syntheses; it has the formula:

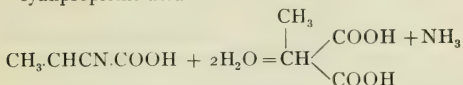


SUCCINIC ACID.—The *normal* succinic acid is obtained by hydrolyzing β -cyanpropionic acid; thus:

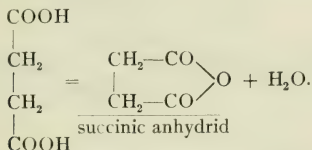


It is prepared by dry-distilling amber, and occurs in gastric contents.

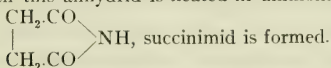
ISOSUCCINIC ACID is obtained by hydrolyzing α -cyanpropionic acid:



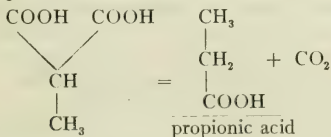
When *normal* succinic acid is heated to 235°C ., it yields *succinic anhydrid* and water:



When this anhydrid is heated in ammonia gas =



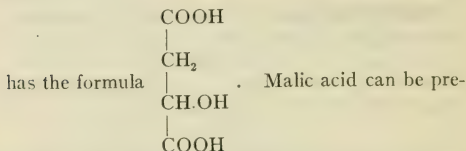
When the *isosuccinic* acid is heated above 130°C ., it decomposes:



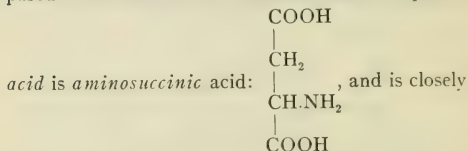
In fact, *any organic acid*, in which two carboxyls are attached to the same carbon atom at high temperatures, splits off CO_2 from one of the carboxyls.

MALIC ACID is found in unripe apples and many

other fruits; chemically, it is *hydroxysuccinic acid*, and



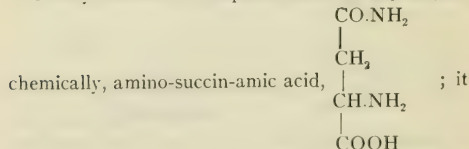
pared from the berries of mountain ash. *Aspartic*



related to malic acid.

Malic acid crystallizes with difficulty; it is soluble in water and alcohol; and iron malate (*ferri pomatum*) is mentioned in the National Formulary; it is a very efficient form of iron when used internally.

Closely related to aspartic acid is *asparagin*,

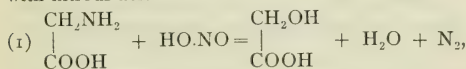


occurs in many leguminous plants; it is soluble in hot water, and with HNO_2 it is converted into malic acid.

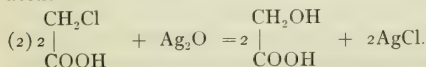
HYDROXYACIDS.

When ethylene glycol is oxidized, *glycollic aldehyd*,
 $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHO} \end{array}$, is formed; this further oxidized yields
 the corresponding hydroxyacid—glycollic acid.

GLYCOLLIC ACID, $\text{CH}_2\text{OH}.\text{COOH}$, occurs naturally in the leaves of the Virginia creeper, wild vine, etc., and is prepared by treating amidoacetic acid with nitrous acid:



or by the action of moist silver oxid on monochloroacetic acid:



The above are two *general reactions* for the preparation of *hydroxy acids*.

Glycollic acid occurs in colorless soluble needles. Chemically, it may be regarded as hydroxyacetic acid.

Substitution of this kind in the paraffin derivatives leads to the possibility of isomerism, as has been stated under Valeric Acid (p. 357), and all the fatty acids beginning with propionic exhibit this possibility. Thus, in propionic acid, $\text{CH}_3.\text{CH}_2.\text{COOH}$, the substitution may take place in the methyl (CH_3) or the methylene (CH_2) group, so that there are two hydroxypropionic acids possible:

β -Hydroxy propionic acid, $\text{CH}_2\text{OH}.\text{CH}_2.\text{COOH}$,

and α -hydroxypropionic acid, $\text{CH}_3\cdot\text{CHOH}\cdot\text{COOH}$ = lactic acid.

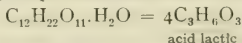
Nomenclature.—For the purpose of identification of the isomerids of this kind, their names are customarily prefixed with letters from the Greek alphabet. Thus, the position where the substitution has occurred is indicated starting with the carbon atom nearest to the carboxyl group. (To understand this, study the formulas of the above two acids.)

LACTIC ACID, α -hydroxypropionic acid, oxypropionic acid, $\text{H}\cdot\text{C}_3\text{H}_5\text{O}$, is a monobasic, monatomic

acid, its graphic formula being

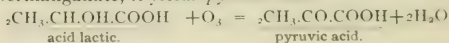
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}\cdot\text{OH} \ ; \ \text{it is} \\ | \\ \text{COOH} \end{array}$$

found in sour milk as product of hydrolysis. Thus, milk-sugar, which is normally present in milk and has the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{H}_2\text{O}$ through the fermentation induced by the lactic-acid ferment (*Bacillus acidi lactici*), is split into lactic acid; thus:



Lactic acid may also be prepared by fermenting starch paste with lactic-acid ferment or by heating cane-sugar with sodium hydroxid.

Lactic may be synthesized from α -aminopropionic acid by one of two general methods given under Glycollic Acid. When oxidized with potassium permanganate, it yields *pyruvic acid*.



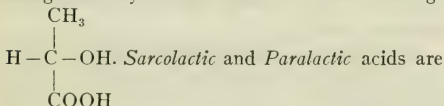
While the synthetic lactic acid is identical in composition and reactions with the acid obtained by fermentation, this latter acid differs in that it is "optically active." It must, therefore, contain an "asymmetric" carbon atom, and more than one form of it should be known.

In reality *three* lactic acids are known:

- (1) Inactive lactic acid (ordinary).
- (2) Dextrolactic acid.
- (3) Levolactic acid.

Properties.—Their chief distinction is the action on polarized light, the crystalline structure of their salts and differences in solubility.

When ordinary lactic acid forms strychnine salts, compounds of both the dextro- and levo-acid are obtained and separated by crystallization. Again, when ordinary mould culture (*penicilium glaucum*) is introduced into solutions of ordinary lactic acid, the levo-acid is destroyed by the bacteria and the dextro-acid remains. The acid is official as a 75% solution (*acidum lacticum*) and its graphic formula showing the "asymmetric carbon" is the following:



found in the muscle and other tissues of the body, also in meat extracts.

CHAPTER XXIX.

DERIVATIVES OF THE ACIDS.

As stated before, acetic acid, when subjected to the action of chlorin, suffers the replacement of the hydrogen atoms of the methyl group CH_3 , yielding three chloracetic acids:

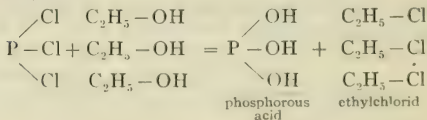
Monochloracetic acid, $\text{CH}_2\text{Cl}-\text{COOH}$, a crystalline compound, melting at 62°C .

Dichloracetic acid, $\text{CHCl}_2-\text{COOH}$, a liquid, boiling at 190°C .

Trichloracetic acid, CCl_3-COOH , prepared by oxidizing the aldehyd-chloral, CCl_3CHO , a crystalline compound melting at 52°C .

What has been said of acetic acid holds true with all the acids of the formic-acid series; the *substitution* always taking place in the *alkyl group* and never in the carboxyl group. These halid derivatives retain the characteristic properties of the acids from which they are derived, since the carboxyl group remains intact.

Acid Chlorids.—When phosphorus trichlorid reacts upon alcohol, it replaces the hydroxyl by a chlorin atom; thus:



This reaction is characteristic of phosphorus chlorid—with all *substances containing the hydroxyl groups*.

When, therefore, an organic acid is treated with this reagent, the hydroxyl residue of the carboxyl group is replaced by chlorin, forming an *acid chlorid* :



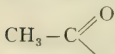
These halid derivatives of the acids are named after the parent acid. Thus, in the above case “acetyl chlorid” with propionic acid we obtain “propionyl chlorid,” etc.

The student should observe the difference in the production of monochloracetic acids and of acetyl chlorid. In producing the first class of compounds, the halogens—chlorin, bromin, etc.—replace the hydrogen of the alkyl, while in the production of acetyl chlorid the phosphorus trichlorid replaces the hydroxyl (OH) in the carboxyl (CO—OH) group by chlorin.

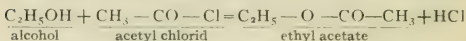
ACETYL CHLORID, $\text{CH}_3\text{—C}\begin{smallmatrix} \text{//} \\ \text{O} \end{smallmatrix}\text{—Cl}$, is a colorless, pungent liquid, fuming in contact with moist air. With water it hydrolyzes into acetic and hydrochloric acids and with alkali hydroxids into corresponding acetates and chlorids.

Acetyl chlorid is a valuable reagent in organic chemistry in that it *reacts with all substances containing the hydroxyl-groups, forming acetyl deriva-*

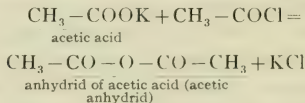
tives. It acts by replacing the hydrogen of the hydroxyl groups by the monovalent *acetyl group*:



Alcohols, therefore, can be converted into alkyl acetates or acetic-acid esters:

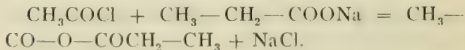


The saturated acids and their alkali salts when treated with acetyl chlorid have their hydrogen of the carboxyl group or the alkali metal replaced by the acetyl group, producing a new class of organic substances, namely, the acid anhydrids:

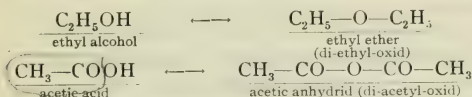


With the higher homologues of acetic acid phosphorus chlorid reacts similarly, producing corresponding chlorids, which resemble acetyl chlorid in properties.

ACID ANHYDRIDS.—These are produced by the interaction of acetyl chlorid and the alkali salts of the acid, as shown above. If we employ the alkali salt of a different acid, a *mixed anhydrid* is produced. Thus, with sodium propionate acetyl chlorid produces acetic-propionic anhydrid:



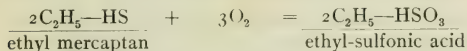
The anhydrids bear the same relation to the acids as the ethers do to the class of alcohols:



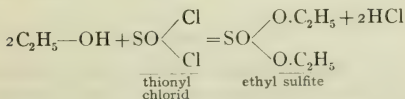
ACETIC ANHYDRID, $(\text{CH}_3\text{—CO})_2\text{O}$, made by a process described above, is a colorless liquid with a pungent acetous odor and a boiling-point of 138°C . It combines with water slowly, forming acetic acid, and with hydroxylic compounds *acetyl derivatives*; thus:



ALKYL-SULFONIC ESTERS AND ACIDS.—When ethyliodid is warmed with sodium sulfite, *ethyl-sulfonic acid* is formed; when ethyl mercaptan is subjected to direct oxidation, the same compound forms:



When thionyl chlorid (SOCl_2) acts upon alcohol, *ethyl sulfite* is formed:



Sulfonic acids possess acid reactions; they form salts with metals and, when treated with phosphorus trichlorid, are converted into alkyl sulfonic chlorids;

thus ethyl-sulfonic acid yields ethyl-sulfonic chlorid, $C_2H_5-SO_2-Cl$. This reaction indicates that the sulfonic acids contain a hydroxyl group.

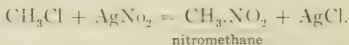
NITROGEN IN ORGANIC COMPOUNDS AND THEIR DERIVATIVES.

In Chapter XXVI the cyanogen derivatives were treated of; all the other nitrogen compounds of pharmaccutic interest will be briefly treated in this chapter.

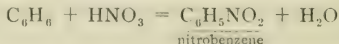
Nitrogen occurs in organic compounds as cyanogen, as nitric or nitrous acids, ammonia, and their derivatives.

Thus, nitric acid enters organic compounds by combining with organic radicals, as, for example, in nitroglycerol. Many of the organic compounds with nitric acid, are explosive.

Nitro-derivatives of the Paraffins include those compounds wherein the NO_2 group replaces the hydrogen of carbon compounds when these are treated with concentrated nitric acid. While the paraffin hydrocarbons can only indirectly have their hydrogen replaced:



Using a paraffin derivative and a salt of nitrous acid, the aromatic hydrocarbons can be treated directly with HNO_3 :

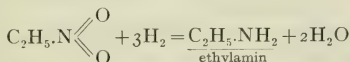


The nitroderivatives, while exhibiting the properties of the ethers of nitrous acid, are far more stable.

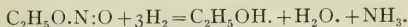
NITROETHANE, $C_2H_5.NO_2$, obtained similarly to nitromethane, is a colorless liquid, with a pleasant ethereal odor, and a boiling-point of $113^\circ C$. In composition, nitroethane is identical with ethyl nitrite, but it differs in structure and properties; thus:



When nitroethane is treated with nascent hydrogen it is reduced to an amin:



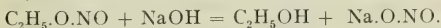
While ethyl nitrite similarly treated, gives ethyl alcohol and ammonia:



When nitroethane is treated with an alkali hydroxid, *sodium nitroethane* is formed:

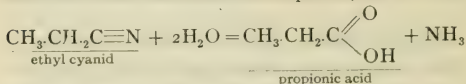


Ethyl nitrite, similarly treated, gives alcohol:

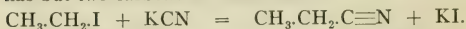


THE NITRILS. In Chapter XXV methyl cyanid, $CH_3.C \equiv N$, was briefly treated. The importance of the nitrils is in the syntheses of the higher carbon compounds. Thus, we can pass from a *one-carbon-*

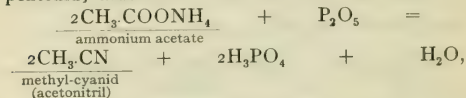
atom compound to a *two-carbon-atom* compound, then to a *three-carbon-atom* compound, etc.:



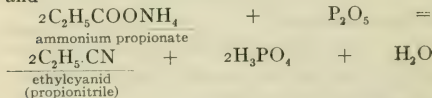
It can be readily seen that propionic acid having three carbon atoms, is a derivative of propane, and yet ethyl cyanid is prepared from ethyl iodid, which has but two carbons in the molecule:



The nitrils can also be obtained by heating the corresponding ammonium salts with phosphorus pentoxid; thus:



and



It will be seen that these nitrils are named after the salts from which derived; thus, *acetonitril*, *propionitril*, etc.

THE ISOCYANIDS.—This class of compounds is also called *carbamins*. Whereas in the nitrils the carbon of the $\text{—C}\equiv\text{N}$ is directly linked to the other carbon atom, in the isocyanids, it is the nitrogen of the group that is linked to the carbon; thus:

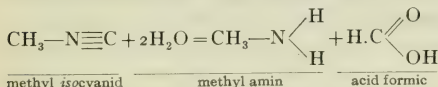


Of all the metals, *silver* alone, instead of a cyanid, forms an *isocyanid*; thus:

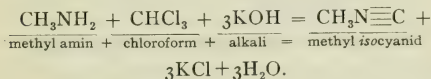


All the other isocyanids may be produced by heating the alkyl iodids with silver cyanid.

When they are treated with water, they are decomposed differently from the other cyanids:

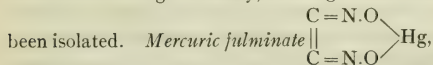


The isocyanids are readily produced by heating together any amin with chloroform and caustic alkali:



Properties.—All the isocyanids are poisonous and all possess a suffocating disagreeable odor.

FULMINIC ACID.—Fulminic acid has the formula CNOH according to theory, although it has never

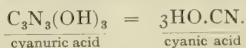


crystallizes with half a molecule of water = $\text{C}_2\text{N}_2\text{O}_2 \cdot \text{Hg} + \frac{1}{2}\text{H}_2\text{O}$. It is prepared by acting with alcohol on a mercuric-nitrate solution in nitric acid. When dry, the salt is a powerful explosive and detonates. It is used in percussion caps, and fired by a fuse, sharp blow or electricity.

CYANIC AND CYANURIC ACIDS.—By fusing together potassium cyanid with lead oxid, *potassium cyanate*, $\text{KO}-\text{C}\equiv\text{N}$, and metallic lead are produced. From this, cyanic acid, $\text{HO}-\text{C}\equiv\text{N}$, may be prepared. It can be crystallized from alcohol, but in aqueous solutions it decomposes into ammonia and carbon dioxid. Cyanic acid can also be prepared from *cyanuric acid*, $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$, which has the graphic formula $\text{HO}-\text{C}=\text{N}-\text{C}-\text{OH}$



Cyanuric acid is obtained by heating urea:



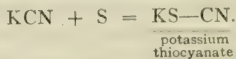
When cyanuric acid is heated, cyanic acid is produced:



Cyanic acid is a strong, unstable liquid which, above 0° , polymerizes rapidly into porcelain-like, opaque mass, called *cyamelide*.

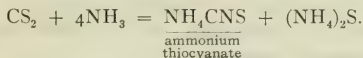
Potassium cyanate, $\text{KO}-\text{CN}$, is also produced when potassium cyanid slowly oxidizes in the air.

THIOCYANIC ACID, $\text{H}-\text{S}-\text{C}\equiv\text{N}$, sometimes called *sulfocyanic*, is obtained in the form of its salts by heating alkali cyanids with sulfur:



Ammonium thiocyanate is obtained by heating

carbon disulfid with ammonia in an alcoholic solution:

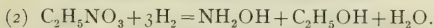
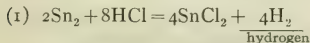


Besides thiocyanic acid, we have the *isothiocyanic acid*, which has the formula $\text{H.N} = \text{C} = \text{S}$; the best known compound of this is *allyl isothiocyanate*, a constituent of volatile oil of mustard (*oleum sinapis volatile*), which should contain not less than 92% of it.

SODIUM NITROPRUSSID, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$, is a valuable reagent for detecting *sulphids*, with which it gives an intense *violet color*. It is prepared by acting with nitric acid on potassium ferrocyanid. It crystallizes in ruby-red prisms, soluble in water.

MERCURIC THIOCYANATE, $\text{Hg}(\text{CNS})_2$ is obtained by adding mercuric chlorid to a solution of potassium thiocyanate. Insoluble powder separates which, on drying, takes fire on ignition, and intumesces with voluminous ash, aggregating in long snake-like tubes—"Pharaoh's serpents." The vapor, containing mercury, is poisonous.

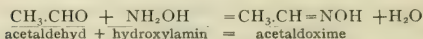
HYDROXYLAMIN, NH_2OH , is obtained by reducing ethyl nitrate with hydrochloric acid and tin; thus:



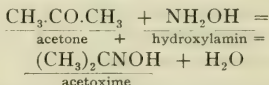
Two forms of alkyl derivatives of hydroxylamin are

known: α methyl hydroxylamin, NH_2OCH_3 , and β methyl hydroxylamin, $\text{CH}_3\text{.NH.OH}$.

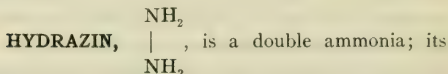
Hydroxylamin is a valuable reagent with the aldehyds and ketones, with which it forms *oximes*, by splitting off water; thus:



It will be observed that the oxime is named after the aldehyd employed; thus, from acetaldehyd we obtained acetaldoxime; likewise, oximes of the ketones are named after the parent ketone. Acetone with hydroxylamin gives:



The oximes are sometimes named *iso-nitroso* compounds.



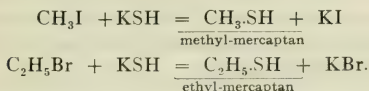
compounds, especially *phenylhydrazin*, $\text{C}_6\text{H}_5\text{NH.NH}_2$, also called *hydrazin-benzene*, is a valuable reagent in organic chemistry, especially in the examination of sugars, with which it forms two well-defined classes of compounds—the *hydrazones* and *osazones*.

THE DERIVATIVES OF SULFUR.

MERCAPTANS or *suljur alcohols*.

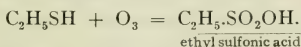
Preparation.—The mercaptans are formed by

treating alkyl halids with potassium hydrogen sulfid; thus:

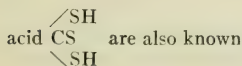
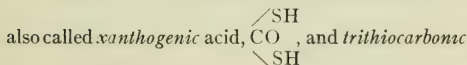
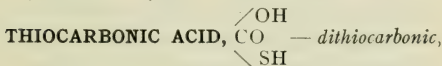
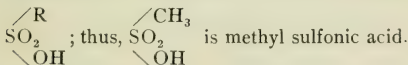


Properties.—Ethyl mercaptan is the most common of the class. They are mostly liquids of a disagreeable, garlicky odor. Similarly with alcohols, mercaptans contain a hydrogen atom replaceable by metals; thus, we have with sodium, a compound, CH_3SNa ; with mercury, $(\text{C}_2\text{H}_5\text{S})_2\text{Hg}$, etc. These compounds are known as *mercaptids*; thus, sodium methyl mercaptid, mercury ethyl mercaptid, etc.

When subjected to oxidation, mercaptans differ from the alcohols in that they *take up* three molecules of oxygen, forming *sulfonic acids*:



The structure of the sulfonic acids may be written—



SULFUR ETHERS.—The *allyl sulfid* (a constituent of oil of garlic), $(C_3H_5)_2S$, mentioned elsewhere is a type of sulfur ethers. They all possess a garlicky odor and all are prepared by acting on potassium sulfid with alkyl halids.

CHAPTER XXX.

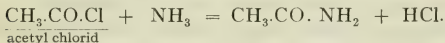
SUBSTITUTION PRODUCTS OF THE ACIDS.

ACID AMIDS are prepared by heating ammonium salts of the corresponding monobasic organic acids in hermetically sealed tubes:

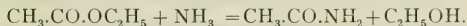


Each molecule of the salt loses a molecule of water. The amids are named after the acids contained in the salt; thus, from ammonium acetate *acet-amid* is produced; from ammonium propionate, *propion-amid*, etc.

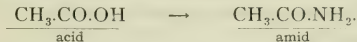
(2) The amids may also be formed by acting with strong ammonia solution on the acid chlorids:



(3) Also by acting with strong ammonia on the esters:

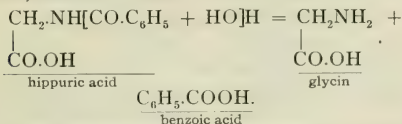


It will be observed that the amids are organic acids in which the hydroxyl group is replaced by the amido, NH_2 , group:



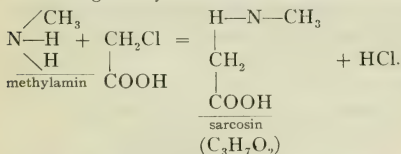
Properties.—Acetamid is prepared by distilling ammonium acetate in a current of dry ammonia. It

hydrochloric acid, benzoic acid and glycin are produced; thus:



The above is the commercial method for producing benzoic acid.

Methyl glycin, “sarcosin,” is obtained by boiling creatin with barium hydroxid—or, synthetically, by condensing methylamin with monochloracetic acid:



Creatin, found in meat-juice with sarcolactic acid, is, chemically, “methyl guanidin-acetic acid,” $\text{C}_4\text{H}_9\text{N}_3\text{O}_2$.

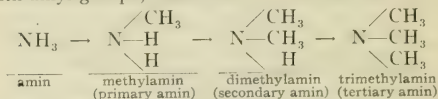
Betain, “trimethyl glycin,” $\text{HO}(\text{CH}_3)_3\text{N.CH}_2\text{.COOH}$, is found in molasses prepared from beets.

Creatinin, $\text{C}_4\text{H}_7\text{N}_3\text{O}_2$, is the anhydrid of creatin, found in small quantities in urine.

Alanin, α -aminopropionic acid, $\text{CH}_3\text{.CH(NH}_2\text{).COOH}$, is a product of the decomposition of silk.

Leucin, α -amino isobutyl acetic acid, $(\text{CH}_3)_2\text{.CH.CH}_2\text{.CH(NH}_2\text{).COOH}$, a product of decomposition of glue and other albuminoid bodies, is obtained from caproic acid.

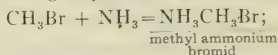
AMINS are strongly *basic bodies* derived from ammonia, NH_3 , by substituting the hydrogen atoms with alkyl groups; thus:



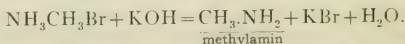
Thus, by substituting one hydrogen atom in ammonia, NH_3 , a primary amin is obtained; by substituting two hydrogens, a secondary amin, and by substituting all three hydrogens, a tertiary amin. We have, therefore, three classes of amins: the *primary*, containing the characteristic group— NH_2 ; *secondary*, containing the group $= \text{NH}$, and tertiary, containing the group $\equiv \text{N}$.

Preparation.—Amins may be prepared:

(1) By treating alkyl halids with ammonia:

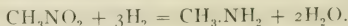


this is decomposed by distilling with alkali-hydroxid:

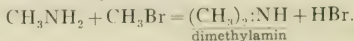


Methylamin is the *simplest* member of the class of *alkaloids*.

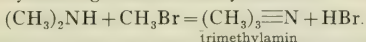
(2) By reducing corresponding nitro-compounds by nascent hydrogen:



Dimethylamin is obtained by treating methylamin with an alkyl halid:

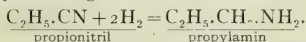


Trimethylamin may be obtained from dimethylamin by treating it with a methyl halid:

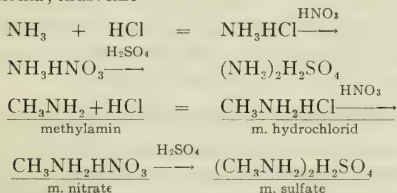


The =NH group of the secondary amins is also called "imido" group, and secondary amins *imido compounds*.

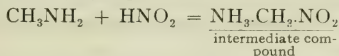
(3) By reducing nitrils:



Properties.—Amins usually possess strong ammoniacal odor, strong alkaline reaction, and are usually soluble in water; they precipitate metals from their solutions, and with acids they form addition products; in these last two properties they are similar to ammonia; thus: like



Identification.—(1) The *primary* amins with nitrous acid lose the amido group which is replaced by the hydroxyl group:



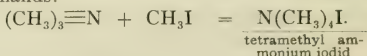
which is hydrolyzed:



(The above is a method of diazotization, whereby an —OH group can be introduced in a compound.)

(2) The *secondary* amins, when heated with alcoholic potash and chloroform, give the *isonitril* reaction (p. 377).

(3) The *tertiary* amins combine directly with alkyl halids:

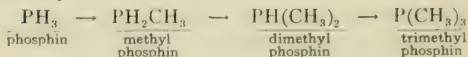


Neither of the other classes of amins afford the reactions given under each class, and these serve, therefore, as means of identification.

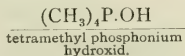
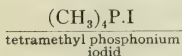
Amins of all three classes have the property of forming double compounds with platinum chlorid analogous to the similar compounds with ammonium and potassium. This property is made use of in quantitatively identifying an amin. Thus, methylaminplatinumchlorid, $(\text{CH}_3\text{NH}_2)_2\text{PtCl}_6$, when ignited, yields 41.5% of metallic platinum.

COMPOUNDS ANALOGOUS TO THE AMINS.

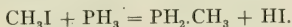
These compounds show the close chemical relationships between nitrogen, phosphorus, antimony and arsenic. They are known as **PHOSPHIN** or phosphonium, PH_3 , **STIBIN** or stibonium, SbH_3 , and **ARSIN** or arsonium, AsH_3 . They may be regarded as derivatives of ordinary phosphin or arsin, etc., and, like the amins, may be *primary*, *secondary* or *tertiary*:



Quaternary phosphonium iodids and hydroxids have likewise been isolated:

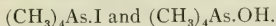


Preparation.—By the action of alkyl iodids on phosphin, etc.:



From the primary, a secondary, and from this tertiary phosphin may be obtained similarly with the amins. All the phosphins are inflammable.

There are no primary or secondary arsins known; the *tertiary arsins*, $(\text{CH}_3)_3\text{As}$, and quaternary arsonium iodids and hydroxids are well-known:



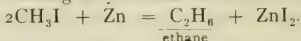
CACODYL is obtained by distilling a mixture of equal parts of arsenous oxid and potassium acetate.

Cacodyl was first obtained by Cadet in 1760, and is contained in "Cadet's liquid." Its composition was ascertained by Bunsen (1837), who named it *cacodyl* (from *kakodus*, stinking) in reference to its intolerable smell. It is exceedingly poisonous, inflammable and has the formula $\text{As}_2(\text{CH}_3)_4$.

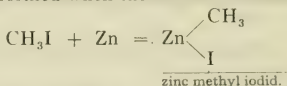
TRIMETHYL STIBIN has the formula $(\text{CH}_3)_3\text{Sb}$, and tetramethyl stibonium hydroxid, $(\text{CH}_3)_4\text{Sb.OH}$, both are known, but both are unimportant.

ORGANO-METALLIC COMPOUNDS.—This term is applied to alkyl compounds of the metals. They resemble nonmetal-alkyl compounds, both in properties and in the method of production.

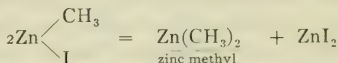
ZINC ALKYL.—Frankland synthesised paraffins (1849) by treating alkyl halids with metallic zinc:



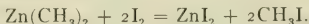
He observed, however, that an additional compound was formed when the zinc was in excess:



When this compound is distilled, zinc methyl is formed:



When halogens act on zinc methyl alkyl halids are formed:



Similarly to zinc methyl, we obtain:

$\text{Hg}(\text{CH}_3)_2$ = methyl mercury;

$\text{Bi}(\text{CH}_3)_3$ = methyl bismuth, and

$\text{Sn}(\text{CH}_3)_4$ = methyl tin, etc.

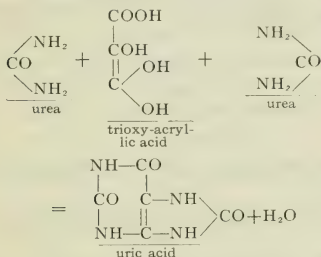
These compounds are very inflammable and volatile.

URIC ACID AND ITS DERIVATIVES.

URIC ACID, $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$, is closely related to urea, both physiologically and chemically. It is almost the chief nitrogenous secretion in many animals, birds and reptiles. In human urine it constitutes in quantity about one-sixtieth that of urea secreted under normal conditions. Uric acid forms three classes of salts—neutral, acid and hyperacid urates.

Of the alkali urates only the potassium and lithium salts are soluble. Lithium urate is the most soluble, while ammonium urate is insoluble.

Formation and Structure.—Uric acid, chemically, is the diureid of trioxycacrylic acid:



It may be made artificially by heating urea with cyanacetic acid.

When uric acid (or a little evaporated urine) is covered with a drop of nitric acid, evaporated to dryness, upon the addition of a drop of ammonia, a beautiful, purplish color (murexide) is developed. *Xanthin* and *guanin* produce the same reaction, but on the addition of a drop of sodium hydroxid the red color turns to blue (distinction from xanthin, etc.).

Concentrated solutions of uric acid reduce Fehling solution.

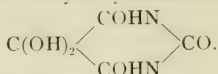
PARABANIC ACID is "oxalyl urea," produced from oxalic acid, urea and phosphorus trichlorid. It

has the formula $\begin{array}{c} \diagup \text{NH.CO} \\ \text{CO} \quad | \\ \diagdown \text{NH.CO} \end{array}$.

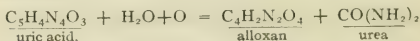
BARBITURIC ACID is prepared by the same reaction from malonic acid, $\text{CH}_2 \begin{smallmatrix} \diagup \text{COHN} \\ \diagdown \text{COHN} \end{smallmatrix} \text{CO}$; the hydroxyl barbituric acid is

DIALURIC ACID, $\text{CHOH} \begin{smallmatrix} \diagup \text{CONH} \\ \diagdown \text{CONH} \end{smallmatrix} \text{CO}$; and

ALLOXAN is dihydroxybarbituric acid,



It is prepared from uric acid by oxidizing it with nitric acid:



XANTHIN, $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$, is closely related to uric acid.

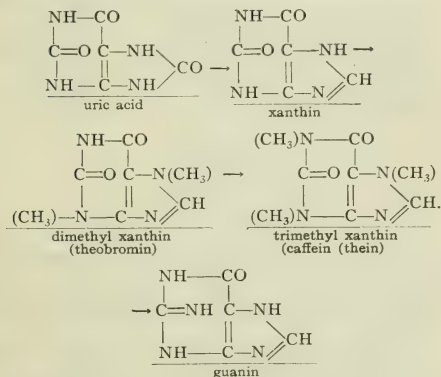
Occurrence.—In both the vegetable and animal kingdoms, in lupine seeds, malt, tea, in meat-juices, etc.

While it contains one oxygen less than uric acid on oxidation, it yields the same products—alloxan and urea.

GUANIN, $\text{C}_5\text{H}_5\text{N}_5\text{O}$, is obtained from guano by extracting it with hot milk of lime, then with sodium carbonate, which extracts the guanin. The product is next precipitated with acetic acid and crystallized from hot dilute hydrochloric acid. Guanin, in structure, is related to xanthin, into which it is converted with nitrous acid. When oxidized, guanin gives *guanidin* (CN_3H_5) and oxalyl urea.

THEOBROMIN, $C_7H_8N_4O_2$, has been synthesized from xanthin. Chemically, it is *dimethylxanthin*. Found in cacao-beans to the extent of 2%.

CAFFEIN and **THEIN**, $C_8H_{10}N_4O_2$, are present in coffee and tea, after which they have been named. Coffee beans contain 1% of caffein, tea leaves from 1.5 to 3% of thein; these bodies are identical and usually classed among the alkaloids. Chemically, *trimethylxanthins*. The relationships of the foregoing compounds may be shown by their structure:



CHAPTER XXXI.

THE CARBOHYDRATES.

Monosaccharoses	Disaccharoses	Polysaccharoses
$(C_6H_{12}O_6)_n$ + Glucose, grape-sugar, or dextrose — Fructose, fruit-sugar, or levulose + Galactose + Mannose — Sorbinose	$(C_{12}H_{22}O_{11})$ + Cane-sugar, or saccharose + Milk-sugar, or lactose + Malt-sugar, or maltose	$(C_6H_{10}O_5)_n$, + Starch + Cellulose — Inulin + Glycogen + Dextrin The gums
<i>Trisaccharose</i> , $C_{18}H_{32}O_{16}$, + Raffinose, or Melitriose		

THE term "carbohydrate," or *carbhydrate*, is applied to a group of natural substances, which, in addition to carbon, contain also hydrogen and oxygen in the proportion in which these unite to form water.

Cane-sugar, $C_{12}H_{22}O_{11}$; glucose, $C_6H_{12}O_6$, and starch, $(C_6H_{10}O_5)_n$, are the familiar carbohydrates.

The carbohydrates are closely related; all the members of the group are alcohols, some, in addi-

Note.—The algebraic signs preceding each name refer to the character of the optical rotation; thus, the minus (—) sign indicates levo-(left-handed) rotary, and plus (+) sign the dextro-(right-handed) rotary sugars.

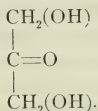
tion, containing aldehyd and ketone groups. Substances which give reactions of two classes of substances are termed "tautomeric."

Carbohydrates containing the aldehyd group are termed *aldoses*; those containing the ketone group, *ketoses*.

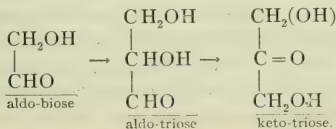
The simplest "*hydroxyaldehyd*," or *aldose*, is glycollic aldehyd, $\begin{array}{c} \text{CH}_2(\text{CH}) \\ | \\ \text{CHO} \end{array}$; the second, glyceric

aldehyd $\begin{array}{c} \text{CH}_2(\text{OH}) \\ | \\ \text{CH}(\text{OH}), \text{etc.} \\ | \\ \text{CHO} \end{array}$ Correspondingly, the lowest

"*hydroxyketone*," or *ketose*, is dioxycetone,



These are regarded as oxidation products of polyatomic alcohols. Their nomenclature consists in the termination "*ose*," and a Greek numeral prefix indicating the number of carbon atoms in the molecule. The above-named carbohydrates may serve as examples:



The necessity for this system is apparent with the higher members which are isomeric; thus, there are four possible aldo-tetroses, eight aldo-pentoses, sixteen aldo-hexoses; besides, there are heptoses, octoses, etc., besides the isomeric ketoses.

The carbohydrates are among the chief products of plant life, and to a small extent also of animal life. We have mentioned the familiar examples, as sugar, starch, etc., from the vegetable kingdom; equally important, however, are milk-sugar, glycogen and frequently grape-sugar derived from the animal organism.

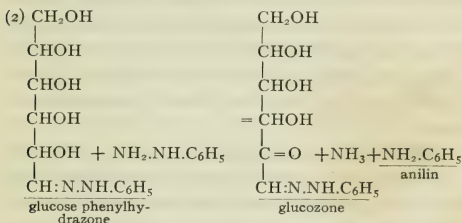
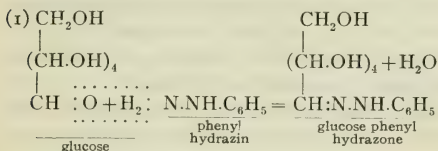
The extensive distribution of the carbohydrates, their extensive use as foods, as materials for the fermentation, fabric, paper and many other industries, makes them very important and interesting.

Classification.—Carbohydrates are naturally divided into those, like sugar, *sweet and soluble*, and into the *tasteless and insoluble*. The sugars are further divided into the *monosaccharids*, containing 6 carbons; *disaccharids*, with 12 carbons, and *trisaccharids*, with 18 carbons in the molecule. Their empiric formula is written $(C_6H_{10}O_5)_n$.

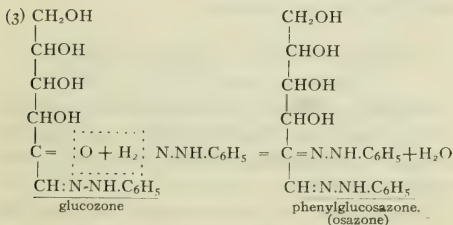
For the important sugars, examine the table at the head of this article.

MONOSACCHAROSES are strong reducers, separating silver from silver nitrate ammonia solution, also reducing Fehling's solution, in this respect acting as aldehyds. With hydrocyanic acid they form cyanhydrin; with phenylhydrazin they form *hydrazones* which, upon treatment with another molecule

of phenylhydrazin, are converted into phenylhydrozone of glucozone, this, with another molecule of the reagent, gives osazone; thus:



It will be seen that the second molecule of the reagent has converted the first compound into a *ketone* ;



The osazones are nearly insoluble in water, well-defined crystals which separate from a solution containing the sugar. They can be readily recognized under the microscope and have a regular definite melting-point by the use of this reagent, it was possible for Fischer (1887 to 1890) to identify, separate and synthesize a number of new sugars.

With hydroxylamin, the *monosaccharoses* give *oximes*, they are readily oxidized, yielding mono- and dibasic acids in the case of aldoses, while the ketoses break up into acids containing fewer carbon atoms. When warmed with nitric acid, they are all converted into oxalic acid, and with hydrochloric into levulinic acids. They are *directly fermentable* with yeast.

DEXTROSE, grape-sugar or *glucose*, $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{CHO}$, occurs naturally in many fruits and sweet plants, either alone or associated with levulose. It has been named "dextrose" in that it rotates polarized light to the right, and "grape-sugar" because it is found in ripe grapes. Grape-sugar may be artificially made by hydrolyzing cane-sugar with dilute hydrochloric acid:



The mixture of dextrose and levulose is known as "invert sugar," and from this grape-sugar may be obtained by crystallizing from hot alcohol in which levulose is soluble.

This inversion of the disaccharoses may also be

brought about by hydrolytic enzymes, invertase and maltase.

Dextrose melts at 86° C., is soluble in water, insoluble in absolute alcohol. The specific rotation $[\alpha]_D = + 52.5$.

LEVULOSE, *fructose*, $\text{CH}_2\text{OH}(\text{CHOH})_3\text{CO}_2\text{H}$, occurs naturally in honey and in ripe fruits, and is produced together with grape-sugar by hydrolyzing cane-sugar. It is best prepared from inulin by hydrolyzing it with dilute acids. It may be isolated from this by boiling with alcohol from which levulose separates in small granular crystals. It melts at 96° C., has the specific rotation $[\alpha]_D = - 93^{\circ}$.

Levulose is soluble in water and alcohol, directly fermentable with yeast, forming alcohol and carbon dioxide; it reduces Fehling's solution. When oxidized, it yields trihydroxybutyric and glycollic acids, each containing fewer carbon atoms than the original sugar, thus proving that it contains the ketonic group:



With phenylhydrazin, it produces *phenylglucosazone*, and with hydroxylamin, an *oxime*.

GALACTOSE, $\text{C}_6\text{H}_{12}\text{O}_6$, is produced together with dextrose by hydrolyzing milk-sugar (lactose). Galactose reduces Fehling's solution, ferments with yeast, with phenylhydrazin it gives *galactosazon*, melting at 193° C.

Galactose crystallizes in fine needles, melting at 163°C .

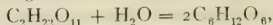
DISACCHAROSES. — CANE SUGAR, sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is found naturally in the sugar-cane, beet, maple and various other plants.

Preparation.—By expressing the juice from the respective plants, neutralizing with lime to remove impurities and to prevent inversion by the plant-acids. The lime is removed by passing CO_2 into the liquid, as calcium carbonate; the liquid is next evaporated *in vacuo* until crystallization occurs. The crude sugar is redissolved, filtered through bone-black to decolorize it, evaporated and recrystallized. The mother liquor, or “residual sugar-house syrup,” is sold as molasses.

Sugar (saccharum) is soluble in water (one-half its own weight), sparingly in alcohol. It melts at 160°C ., at higher temperatures it darkens, and finally carbonizes into a dark brown syrup, known as burnt sugar or “caramel.”

Sucrose has the specific rotation $[\alpha]_{\text{D}} = + 66.5^{\circ}$; the rotary power of sugar is made use of in determining its sucrose content.

Sucrose is *not directly fermentable* with yeast, but after inverting with dilute acids into glucose,



it ferments into alcohol and carbon dioxid.

Sucrose does not reduce Fehling's solution, nor does it react with phenylhydrazin or hydroxylamin, showing that it contains neither the aldehydic nor ketonic group.

LACTOSE, *milk sugar*, $C_{12}H_{22}O_{11} \cdot H_2O$, is a natural constituent of milk.

Preparation.—By removing the curd from milk by means of rennet, evaporating the “whey,” filtering through bone-black and crystallizing.

Lactose (*saccharum lactis*) is harder than sucrose and therefore valued for its attrition properties in the preparation of triturations of energetic drugs, in the making of tablets and pills. Lactose is less soluble than sucrose and maltose, it has the rotation $[a] D = +80^\circ$.

Lactose reduces Fehling's solution; is *not directly fermentable* with yeast; it reacts with phenylhydrazin. When boiled with dilute acids, it hydrolyzes into dextrose and galactose. When sprinkled upon strong H_2SO_4 , it should not immediately darken (absence of sucrose).

MALTOSE, *malt sugar*, $C_{12}H_{22}O_{11} \cdot H_2O$, is obtained from the “wort” extracted from malt—“sprouted barley,” and produced by the action of “diastase” upon starch. This is the object of “malting” barley; the diastase at a favorable temperature hydrolyzes the starch in the moist grain into sugar.

Maltose crystallizes in small white crystals; it is very soluble in water, and has the rotation $[a] D = +140^\circ$ —It is *directly fermentable* with yeast. It reduces Fehling's solution; with phenylhydrazin it forms crystalline phenylmaltosazon. Its other reactions indicate that it is an aldehydic sugar.

RAFFINOSE, $C_{18}H_{32}O_{16} + 5H_2O$, is a tasteless sugar found in the sugar-beet. When boiled with

dilute acids it hydrolyzes into glucose, galactose and levulose.

POLYSACCHAROSES.—STARCH (*amylum*) is a constituent in the cells of many plants, it is usually stored in the underground stems, as potato, or in seed, as maize or wheat, etc. In Europe, starch is mainly prepared from potatoes; in America, from maize, and in India, from rice. The process of starch-making consists in grinding the tubers or seeds, washing with a stream of cold running water, which, holding the starch grains in suspension, is run off into deposit vats, where the starch deposits as a paste, which is washed and dried.

The microscopic appearance of the different starches is such as to determine its source, this is a valuable property in detecting starches in powdered drugs, of which they are frequent adulterants.

Starches occur in a white, amorphous powder, insoluble in water, but upon boiling the granules swell slightly, burst and partially dissolve. The soluble portion is called *granulose*; the insoluble, starch cellulose. Starch is colored blue with iodine. When boiled with nitric acid, *dextrin* (British gum) is produced. Dextrin dissolves in water, furnishing a valuable mucilage, which may also be used for saponification purposes. When further heated, dextrin is finally converted into dextrose.

The constitution of starch is at the present time unknown; its empiric formula is usually written $(C_6H_{10}O_5)_n$.

INULIN, $(C_6H_{10}O_5)_3$, is a substance replacing the

starch granule in the cells of the compositæ. It is a white powder, soluble in hot water, colored yellow with iodine, and when hydrolyzed with dilute acids it is converted wholly into levulose.

GLYCOGEN, $(C_6H_{10}O_5)_n$, is a carbohydrate occurring in the liver of mammals. It is a white powder, soluble in boiling water, colored brown with iodine; when boiled with dilute acids, it is hydrolyzed into dextrose, while with diastase it becomes a maltose.

CELLULOSE, $(C_{12}H_{20}O_{10})_n$, is the principal constituent of the cell-walls of plants. While the cell walls of young plants consist almost entirely of cellulose, as these become older this is replaced by *lignin* and such other material as wax, gum, etc.

Pure cellulose (*gossypium purificatum*) can be prepared from plant fibers, such as raw cotton, by washing it with ether to remove the waxes; next, with alkali carbonate to remove gum; then with hydrochloric acid to destroy the lignin, and finally with weak alkali hydroxid to neutralize the acid.

In this way *absorbent cotton*, which is the purest form of cellulose, is produced.

Pure cellulose occurs in a white amorphous mass, insoluble, but dissolved by ammoniacal copper sulfate solution, from which it may be reprecipitated in the form of a gelatinous mass by acids. By treating cellulose with strong sulfuric acid, a semitransparent mass of "vegetable parchment" is obtained. By dipping paper into a mixture of two volumes sulfuric and one volume of water, the paper becomes

tough and translucent. Washed free from the acid and dried, it constitutes *parchment paper*.

Strong alkali solutions produce gelatinization and thickening of the walls of vegetable fiber, followed by contraction. Advantage is taken of this fact in dipping cotton fiber and cloth, in that it produces *crinkled* or *mercerized* surfaces.

Nitric acid acts upon cellulose, rapidly producing a series of cellulose nitrates known as *nitrocelluloses* or *pyroxylics*. These substances are not true nitrates, but rather nitric esters of cellulose. The *hexanitrate* is known as *gun-cotton*.

NITROCELLULOSE.—The hexanitrate, $C_{12}H_{12}O_4(O.NO_2)_6$, is the true, *highly explosive* gun-cotton. It is prepared by macerating pure cotton in a mixture of 3 parts fuming nitric acid and 1 part strong sulfuric acid for 24 hours, at a temperature not exceeding $10^\circ C$. It is next removed, washed free from the acid and carefully dried at low temperature. When compressed into cartridges it can be detonated and forms a powerful explosive. The hexanitrate is insoluble in a mixture of ether-alcohol, but forms a transparent jelly. This jelly with nitroglycerin constitutes the powerful explosive *cordite*.

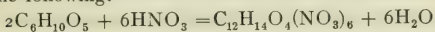
The hexanitrate dissolved in nitroglycerin constitutes *blasting gelatin*.

Soluble gun-cotton, $C_{12}H_{16}O_6(NO_3)_4$, pyroxylinum, *pyroxylin*, tetranitrocellulose, consists chiefly of cellulose tetranitrate. It should be kept in cartons, protected from the light. A yellowish-white, matted mass of filaments, resembling raw cotton. Exceed-

ingly inflammable, burning with a rapid, luminous flame, slowly but completely soluble in 25 parts of a mixture of alcohol (1 vol.) and ether, (3 vols.), (collodion); also in acetone (liquid skin) and in glacial acetic acid; and precipitated from these solutions on addition of $(\text{NH}_4)_2\text{S}$, gives *raw, artificial silk*. Gun-cotton is prepared from cellulose in which four OH groups have been replaced by four NO_3 groups; thus:



This is the official or "soluble gun-cotton," while the following:



constitutes the hexanitrate which is the true explosive guncotton described above, and is insoluble in the mixture of alcohol and ether. From pyroxylin the *collodion* of the Pharmacopœia is prepared (4%).

CELLULOID, xylonite, is a substance made from pyroxylin and camphor by dissolving the former in the latter by fusion. When coloring matter is added, delightful tints are produced. This fused mass is pressed powerfully into appropriate moulds, furnishing many appurtenances of domestic and industrial utility.

DEXTRIN (British gum).—Two varieties of this substance are known—the white and the yellow. It is obtained by boiling starch with water acidulated with sulfuric or nitric acids. Employed as a mucilage, which is a good emulsifying agent.

EXTRACTION OF VEGETABLE DRUGS. *Based on the Insolubility of Cellulose.*—A very important

principle in pharmacy is attached to the insolubility of cellulose in inorganic solvents: Cellulose forms the bulk of inert plant-matter and, being insoluble in ordinary solvents (alcohol and water), principles soluble in these solvents can readily be separated from it. Solvents used for the extraction of proximate principles (alkaloids, glucosids, resins, oleoresins, organic acids, volatile oils, fixed oils, waxes, coloring matters and various aromatic principles, etc.) are known as *menstrua* (sing., *menstruum*).

PAPER (*charta*) is prepared directly from cellulose in the form of wood, straw or linen rags by heating in revolving cylinders with alkalis, steam and, under pressure, beating into a pulp and bleaching with chlorin gas. The pulp is transferred to endless felt-belting, revolving on heated cylinders to dry and the sheets are finally pressed between hot rollers to give them a smooth or "calendered" surface. Paper to which glue or talcum has been added to produce a gloss and high finish is called "sized." Paper to which no similar substances have been added is called "unsized" paper, and is the kind directed for the official paper.

SUBERIN is a modification of cellulose and constitutes *cork*.



CHAPTER XXXII.

CYCLIC OR AROMATIC HYDROCARBONS AND THEIR DERIVATIVES.

Also called carbocyclic, or closed-chain, compounds, and frequently **BENZENE SERIES**.

When coal-tar is subjected to destructive distillation, the distillate produced upon standing separates into two layers.

The upper layer is a dark brown, aqueous liquid, containing ammonia and ammonium sulfid, the lower layer consists of "coal-tar."

When the coal-tar is in turn subjected to distillation, two fractions are obtained—the volatile, a brown, oily liquid, and a residue of coal-tar pitch, commonly known as "asphaltum."

When asphaltum is further distilled, it yields chrysene, pyrene, etc. (commercially not valuable), and a residue which is "coke."

If, now, the brown, oily liquid be subjected to fractional distillation, it can be separated into two portions, one of which floats upon water and is, therefore, known as "light oils," and a second fraction possessing a higher specific gravity than water and in which it will sink, known as "heavy oils."

The "light oils" contain three different classes of compounds:

(1) *Hydrocarbons*, as *benzol*, *toluol*, *three xylols*, *ethyl benzene*, *mesitylene*, *pseudocumene*, *terpene*, *naphthalene dihydrid*, *diphenyl*, *methyl anthracene*, also *hydrocyanic* and *acetic acids*.

(2) *Oxygenated substances* allied to the alcohols, as *phenol*, *ortho-*, *meta-* and *paracresols*, *xylenol*, etc.; and,

(3) *Basic compounds* similar to the amins, as *pyridin*, *pyrrol*, *anilin*, *quinolin*, etc.

The second class, or oxygenated substances, can be removed by shaking the "light oils" with a solution of soda, with which sodium phenolates, etc., will form, while the basic compounds can be removed by treating the "oils" with dilute acids.

The residue left after the second treatment is a mixture of hydrocarbons, which are the starting-point of a new homologous series of aromatic compounds, are separable into its constituents by fractional distillation, etc.

Coal-tar is the chief source of benzene.

It is a by-product in gas manufacture. Bituminous coal yields most coal-tar, while anthracite coal yields least.

The coal is subjected to destructive distillation in the process of gas making in fire-clay retorts, 6 to 8 feet long and 10 wide. Iron retorts were formerly employed for this purpose, but this metal, being readily attacked by sulfur, has been substituted by fire-clay.

When coal is subjected to destructive distillation, the degree of heat employed has a great influence

upon the percentage and character of the fractions; thus:

At	High temperatures.	Low temperature.	
<div> <div>Volatile matter or <i>gas</i>.</div> <div>Nonvolatile matter or <i>coke</i>.</div> </div>	Gas,	20.5%	6.5%
	NH ₃ H ₂ O,	3.1%	7.2%
	Tar,	17.1%	26.5%
	Sulfur,	3.0%	
	Water,	4.2%	
	(above 100% C.,	47.9%	40.2%
	Fixed carbon,	45.0%	50.0%
	Sulfur,	0.3%	
	Ash,	6.8%	9.0%
		100.0 parts.	99.2 parts.

A ton of coal furnishes the following products of destructive distillation: 11,000 cubic feet of gas and 9 gallons of tar.

ILLUMINATING GAS is composed of hydrogen, marsh gas, carbon monoxid, heavy hydrocarbons, hydrosulfuric acid, ammonia, etc. When subjected to purification by being passed first through water and then through burnt lime (CaO) or iron hydrate and lime, its composition changes; thus:

	Before purification.	After purification.
H,	47%	51%
CH ₄ ,	34%	36%
CO,	5%	5%
Heavy hydrocarbons,	4%	4%
H ₂ S,	1%	none
NH ₃ ,	1%	none
CO ₂ ,	4%	none
N,	4%	4%
	In 100 parts.	In 100 parts.

To enrich the gas or "carburette" it, higher hydrocarbons are employed, such as naphtha,

benzene, naphthalene, etc.; naphthalene cannot be used to advantage in the winter time, as it freezes out.

FRACTIONS OBTAINED BY DESTRUCTIVELY DISTILLING COAL.

The fraction that passes below 80° C. is gas.

The fraction that passes between 80 and 170° C. constitutes "light oils."

The fraction that passes between 210 and 270° C. is composed of creasote oil, middle oil (phenol), naphthalene, and constitutes the "heavy oils."

The fraction passing above 270° C. is chiefly *anthracene*.

The "light oils" come over to the extent of 2 to 4%, when they are fractionated; "*dead oil*" is left behind.

The "heavy oils" are found to the extent of 32 to 35%, and coke to the extent of 45%.

The "heavy coal-tar oil" is not further purified, but since it possesses antiseptic properties on account of the phenols it contains, it is used as a preservative for telegraph poles, for piles for bridges, for railway-sleepers and timber in general.

The light oils possess an unpleasant odor, and quickly acquire a brown color by absorbing oxygen from the air; by shaking with H_2SO_4 , however, these oxidizable bodies are charred into a tarry mass and can be removed.

The separation of the constituents of the different fractions will be described together with the discussion of the substances themselves.

BENZENE.

Benzene is sometimes called benzol, phenyl-hydrid, coal-tar benzin; its chemical formula is C_6H_6 , or C_6H_5H (Faraday, 1825); it has a boiling-point, of $80.5^\circ C$. Specific gravity, 0.9 at 0° , 0.87 at 25° .

Preparation.—From coal-car it is obtained by the fractional distillation of the "light oils."

The fraction boiling between 80° and $150^\circ C$. is employed for the preparation of benzene and its homologues.

The homologues are removed by agitation with strong H_2SO_4 .

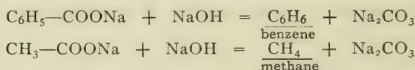
The acid removes anilin, pyridin, etc.; when it is withdrawn, the "oils" are treated with strong solution of caustic soda which unites with the phenol, forming sodium phenolate and neutralizes the residual sulfuric acid. When the soda solution is drawn off, the residual oil is washed with water and, so purified, subjected to fractional distillation in apparatus heated by steam and provided with a long fractionating column.

The fraction which is first collected is known as a "50% benzene" or as a "90% benzene." These terms signify a benzene in mixture of its higher homologues as toluene and xylene. They indicate that at $100^\circ C$., 50% of the liquid will distill over in the case of the *fifty per cent.* kind; and 90% in the case of the *ninety per cent.* kind. The fractions having higher boiling-points are known as "solvent naphtha," used as a solvent in the rubber industry,

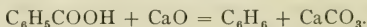
in water-proofing fabrics and for illuminating purposes.

The "50%" and "90%" benzenes, by a second fractional distillation, are separated into benzene, toluene, xylene and thiophene (C_4H_4S).

Synthetic Production.—(1) Benzene may be synthesized by treating sodium benzoate with caustic soda, just as methane is prepared from sodium acetate and caustic soda; thus:



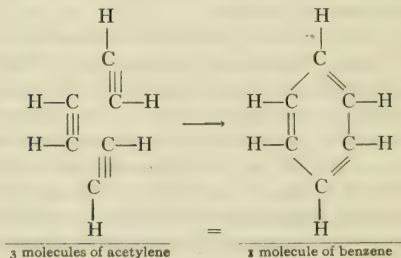
(2) By heating benzoic acid with lime:



(3) By heating acetylene to redness in a tube of hard glass, when it polymerizes (Berthelot):



Benzene is, therefore, a polymer of acetylene, and on this polymerization the graphic structure of benzene may be based; thus:



When benzene is heated in a red-hot tube, it is reconverted into acetylene (not very completely).

Properties.—When cooled to 0° C., benzene solidifies to a solid mass which melts at 6° C. It is insoluble in H_2O , but soluble in other solvents; it burns with a sooty flame, and is a good solvent for fats, resins, sulfur, iodine, etc. Its chief impurity, *thiophene*, is separated from it by adding concentrated H_2SO_4 , freezing it, and then pouring off the charred impurities from the crystalline mass.

Benzene combines with 2, 4 and 6 hydrogen atoms, forming *additive* compounds, as benzene hexahydride, C_6H_{12} (also found in Russian petroleum). With the halogens it forms different *substitution* compounds.

The difference between these two classes of derivatives should be clearly distinguished: *additive* compounds are named similarly to the inorganic compounds; thus, *benzene dichloride*, $\text{C}_6\text{H}_6\text{Cl}_2$, corresponds to mercury dichloride, HgCl_2 . Whereas *substitution* compounds are distinguished by attaching the names and numerical proportions of the substituting bodies to the parent substance; thus, $\text{C}_6\text{H}_4\text{Cl}_2$ corresponds to *dichlorobenzene*.

Additive Compounds.

Benzene hexahydride = $\text{C}_6\text{H}_6\text{H}_6$

Benzene hexachloride = $\text{C}_6\text{H}_6\text{Cl}_6$

Benzene tribromide = $\text{C}_6\text{H}_6\text{Br}_3$

Substitution Compounds.

C_6Br_6 = hexabromobenzene.

C_6Cl_6 = hexachlorobenzene.

$\text{C}_6\text{H}_3\text{I}_3$ = triiodobenzene.

CONSTITUTION OF BENZENE.

Kekulé (1866) was the *first* to propose the hexavalent benzene nucleus. That is to say, three of the four carbon bonds are used up in linking with

adjacent carbon atoms, and the fourth bond is united with hydrogen or other elements or groups of elements.

Secondly, he showed that the six hydrogen atoms are *equi-valent*; that is, when either one is substituted by another atom, one, and *only one*, derivative can be obtained. And in reality *there are no isomeric monosubstitution compounds* of benzene.

Thirdly, that *only three disubstitution compounds can exist*, and in reality only three have ever been prepared.

This has been equally true when both the substituting groups are the same, as in dimethylbenzene, and when both the groups are different, as in methyl-amido benzene.

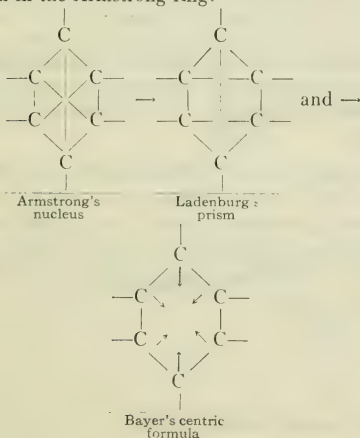
Fourthly, that with three similar substituting groups *only three isomeric trisubstitution derivatives are possible*, and in reality *only three* trisubstitution products of benzene *are known*.

In *opposition to Kekulé's theory*, some chemists hold: *First*, that unsaturated compounds of the fatty series in which the olefinic linking (double-bond) is assumed, such as ethylene, allyl alcohol, etc., possess the property of forming with bromin addition compounds at the ordinary temperature without splitting off hydrogen and forming hydrobromic acid, which fact is in contradistinction to the paraffinic linking (single bond) in which the hydrogen is split off with the formation of substitution compounds. Thus, if Kekule's assumption were correct, six bromin atoms would unite directly with benzene under ordinary conditions, which, however, occurs

only in *direct sunlight*, therefore not without the aid of active force. *Secondly*, there must be possible, according to Kekule's theory, two orthodisubstitution derivatives; one of them where the adjacent two carbon atoms are linked by a double bond:

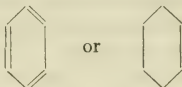


Others suggested benzene nuclei in which the alternate single and double bonds are done away with, and nine single bonds introduced instead, as the one shown in the Armstrong ring:

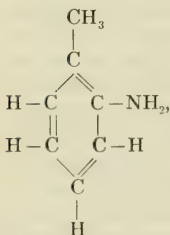


in which each carbon is united with two carbons and one hydrogen, thus linking three bonds, while the fourth bond is called the *centric*, *potential* or *residual*, which is portrayed by an arrow pointing to the center and signifies a modified bond of a somewhat ill-defined character.

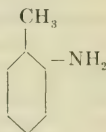
Chemists have for these many reasons been forced to relinquish the Kekulé formula and, wanting further proof to establish the others proposed, avoid any hypothesis concerning the structure of benzene nucleus, adhering to the simple hexagon formula:



each angle of which is assumed to represent a carbon and a hydrogen atom, and only the groups which substitute the hydrogen, are represented; thus, in stead of

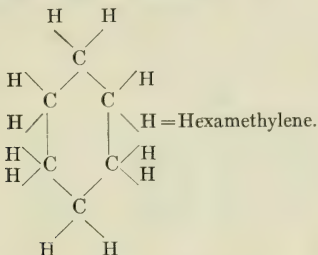


the following

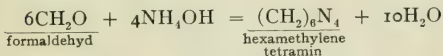


stands for methyl-amido benzene.

When each carbon of the nucleus is linked with two hydrogens, we have the formula of



Hexamethylene is unimportant, but its amin-derivative, which is obtained by evaporating a solution of formic aldehyd and ammonia, is important; thus, we condense:



HEXAMETHYLENEAMIN (hexamethylamina U.S. P.), is a crystalline substance sold under various names, as cystogen, formin, aminoform, urotropin, etc. Soluble in water. Employed as antiseptic in purulent affections of kidneys and bladder.

SATURATED HYDROCARBONS OF THE BENZENE SERIES.
(C_nH_{2n-6})

	Name	Specific gravity	Boiling-point
C_6H_6 C_7H_8	Benzene, C_6H_6 , Toluene, $C_6H_5\cdot CH_3$,	0.899 (0°) 0.87 (20°) 0.882 (0°) 0.865 (20°)	80.5° 111°
C_8H_{10}	{ Xylenes, $C_6H_4(CH_3)_2$, Ethyl benzene, $C_6H_5(C_2H_5)$,	0.876 (20°) 0.865 (20°) 0.863 (20°) 0.883 (0°)	o-b.p., 142° m-b.p., 139° p-b.p., 137° 134°
C_9H_{12}	{ Trimethyl benzenes, $C_6H_3(CH_3)_3$, 1, 3, 5, Mesitylene, (s), 1, 2, 4, Pseudocumene, (a), Hemellithene, (v), Methylethyl benzenes, $C_6H_4(CH_3)(C_2H_5)$ or, Ethyl toluenes: Normal propyl benzene, $C_6H_5(C_3H_7)$, Isopropyl benzene (cumene),	0.878 (20°)	160° 169° 175° o-b.p., 160° m-b.p., 159° p-b.p., 162° 158° 153°

SATURATED HYDROCARBONS OF THE BENZENE SERIES.—*Continued.*
(C_nH_{2n-6})

	Name	Specific gravity	Boiling-point
$C_{10}H_{14}$	<p>{ Tetramethyl benzenes, $C_6H_2(CH_3)_4$, s- = Durene, a- = Isodurene, v- = Prehnitene, Dimethylethyl benzenes, $C_6H_3(CH_3)_2(C_2H_5)$, Six isomers possible. Diethyl benzenes (3) $C_6H_4(C_2H_5)_2$. Cymene, $C_6H_4(CH_3)(C_3H_7)$ Six isomers possible. Butyl benzenes, $C_6H_5(C_4H_9)$ Four isomers possible. Pentamethyl benzene, $C_6H(CH_3)_5$, Amyl benzene, etc., $C_6H_5(C_5H_{11})$. { Hexamethyl benzene, $C_6(CH_3)_6$, Triethyl benzene, etc., $C_6H_3(C_2H_5)_3$.</p>	0.856 (20°)	<p>m.p., 79° b.p., 190° b.p., 195° m.p., 4° b.p., 204°</p> <p>b.p., 175°</p>
$C_{11}H_{16}$			<p>m.p., 51° b.p., 231°</p>
$C_{12}H_{18}$			<p>m.p., 164° b.p., 264°</p>

CHAPTER XXXIII.

BENZENE DERIVATIVES.

OF the twenty-seven aromatic hydrocarbons given in the table, only the first four are found in coal-tar:

Benzene, C_6H_6 , or benzol.	Synonyms.	Structure.
Toluene, C_7H_8 , or toluol	= methylbenzene,	$C_6H_5CH_3$
Xylene, C_8H_{10} , or xylol	= dimethylbenzene,	$C_6H_4(CH_3)_2$
Cumene, C_9H_{12} , or cumol	= trimethylbenzene,	$C_6H_3(CH_3)_3$

The higher homologues can all be formed by synthesis. While but one benzene and one toluene are known, the higher hydrocarbons form several isomers.

Properties.—The closed-chain hydrocarbons are acted on more easily by strong sulfuric and nitric acids than the paraffins. The aromatic derivatives are more resistant to oxidizing agents.

When nitrous acid is allowed to act on the aromatic amines, diazo compounds are formed: *Diazo compounds* exhibit two nitrogen atoms linked together; to these is linked a radical by two bonds, and one bond remains free.

The aromatic hydrocarbons, similarly with the aliphatic, form alcohols, aldehyds, ethers, ketones, halid derivatives, amines, nitro compounds, acids, etc.

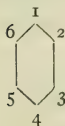
When benzene is treated by bromine, it forms a substitution product—*monobrombenzene*, C_6H_5Br ; monobrombenzene, in turn, when acted upon by nitric acid, forms nitrobrombenzene, $C_6H_4.NO_2.Br$.

Thus, C_6H_6 had one of its six hydrogens replaced by Br, and another one by the $-NO_2$ group. If we now treat nitrobrombenzene with nascent hydrogen, we can remove the bromine and obtain nitrobenzene, $C_6H_5.NO_2$, in which the nitro group is easily replaced by bromine, again forming monobrombenzene, C_6H_5Br .

Without going into much detail, the above plainly explains how it is possible to know that in replacing successive hydrogens in benzene a different hydrogen atom is replaced in each reaction.

Thus, in the monobrombenzene produced, by replacing the $-NO_2$ group with bromine, *we have certainly replaced a different hydrogen atom from that replaced in the first reaction.* The two monobrombenzenes, however, are *identical*—proving that *only one monosubstitution benzene can exist*, and in reality the *mono-substituted benzenes have no isomers.*

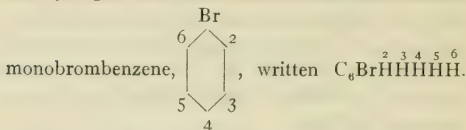
The above examples of the substitution of benzene can be further made plain by assuming that each angle of the benzene nucleus contains *one carbon atom* in combination with *one hydrogen atom*; and that each carbon and hydrogen can be numbered consecutively, starting at the top of the ring:



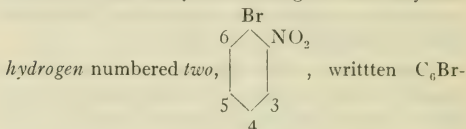
. If, in addition, we represent benzene by

$\overset{1}{C_6}H,\overset{2}{H},\overset{3}{H},\overset{4}{H},\overset{5}{H},\overset{6}{H}$, we can begin to argue out the

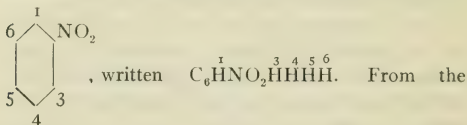
substitution. Let us assume that bromin substituted the *hydrogen* numbered *one*, we will then have a



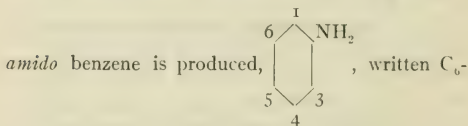
This product treated with nitric acid will yield us nitrobrombenzene by substituting the next adjacent



By treating the above compound with hydrogen, the bromin is removed and nitrobenzene produced,

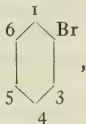


above it is plain that the hydrogen numbered *one* has been reestablished. If we now attempt further reduction of nitrobenzene with hydrogen,



$\overset{1}{\text{H}}\text{NH}_2\overset{3}{\text{H}}\overset{4}{\text{H}}\overset{5}{\text{H}}\overset{6}{\text{H}}$, which by treatment with bromin is

again converted into monobrombenzene,



written $\text{C}_6\overset{1}{\text{H}}\text{Br}\overset{3}{\text{H}}\overset{4}{\text{H}}\overset{5}{\text{H}}\overset{6}{\text{H}}$, and showing that a *different hydrogen* has been replaced in this last reaction than in the first. Therefore, it is safe to assume that if the replaceable hydrogen atoms are equivalent, the six carbon atoms must be united into a *closed chain* which is *stable* and *hard to break up*.

ISOMERISMS.

(1) Assuming Kekulé's hypothesis of the closed benzene ring, we can have *one only monosubstituted benzene* irrespective of which hydrogen atom was replaced.

(2) We find *three disubstitution products*:

Replacing the hydrogens 1, 2 or 1, 6, named *ortho*-position; replacing the hydrogens 1, 3 or 1, 5, named *meta*-position; replacing the hydrogens 1, 4, named *para*-position, in which the replacing groups are *adjacent* or *vicinal*, as in the *ortho* (abbreviated-o), *alternate* as the *meta* (abbreviated-m), or *opposite* as in the *para* (abbreviated-p) position.

(3) Where the substituting *groups* are *all alike*, we have *three trisubstitution products*:

Replacing hydrogens 1, 2, 3, named *consecutive* or *adjacent*; replacing hydrogens 1, 3, 5, named *symmetric*; replacing hydrogens 1, 2, 4, named *asymmetric* or *irregular*.

(4) There can be *six trisubstitution compounds*, of *two substituting groups*.

(5) There can be *ten trisubstitution compounds*, of *three substituting groups*.

(6) There can be *three tetrasubstitution products* where the substituting groups are alike:

Replacing hydrogens 1, 2, 3, 4, named *consecutive*; replacing hydrogens 1, 2, 4, 5, named *symmetric*; replacing hydrogens 1, 2, 3, 5, named *asymmetric* or *irregular*.

(7) There are *seven tetrasubstitution compounds*, of *two substituting groups*.

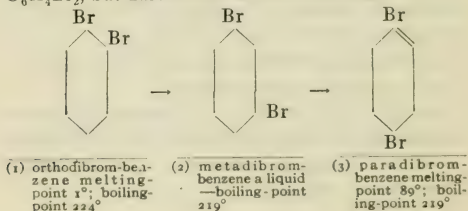
(8) Sixteen *tetra compounds*, with *three substituting groups*.

(9) *Thirty tetra compounds* with *four substituting groups*.

(10) There is but *one penta-substitution product*, just as there is but one *hexa substitute*.

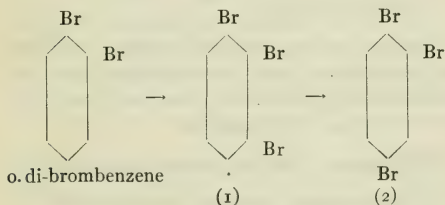
IDENTIFICATION OF DISUBSTITUTED BENZENES.

Taking dibrombenzenes as example, we have three, all having the same molecular formula, $C_6H_4Br_2$, but different structural formulas:

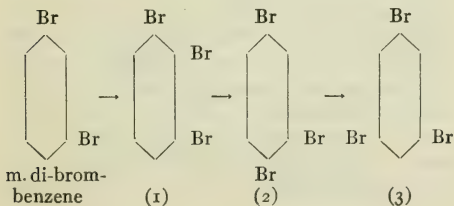


It will be seen that while (1) is different from (2) and (3) in its boiling-point, the latter two are identical, both boiling at 219° C.; but (3) solidifies at 89° C. and is ordinarily a *solid*, while (2) is always a *liquid*.

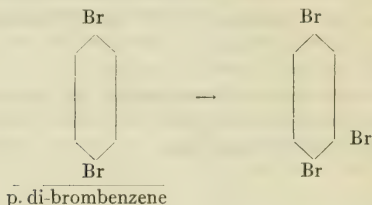
By converting the dibrombenzenes into tribrombenzenes, we can obtain from *the ortho* but *two trisubstitution* benzenes; thus:



From the *meta* three trisubstitution benzenes can be obtained; thus:



From the *para* but *one* trisubstitution benzene can be obtained; thus:

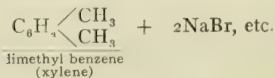
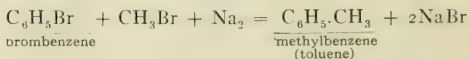


Therefore, *ortho* compounds are those furnishing *two* trisubstitutes; *meta* compounds are those furnishing *three* trisubstitutes; *para* compounds are those furnishing *one* trisubstitute.

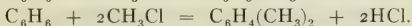
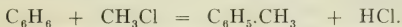
SYNTHESIS OF THE BENZENE HOMOLOGUES.

The homologues of benzene are synthesized in a way similar to the preparation of the methane homologues by either of two following reactions:

(1) *Fittig's reaction* is brought about when halid derivatives of benzene or one of its homologues and an alkyl halid in ethereal solution are treated with metallic sodium or potassium:



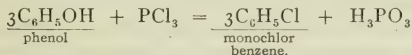
(2) *Friedel and Craft's reaction* consists in adding anhydrous aluminum chlorid to a mixture of an aromatic hydrocarbon and an alkyl chlorid; corresponding homologues are formed and hydrochloric acid evolved; thus:



Properties.—The benzene homologues are volatile, oily liquids, insoluble in water, soluble in alcohol and ether. They form two classes of derivatives: (a) when the substituting group replaces hydrogen in the benzene nucleus and (b) when it replaces hydrogen in the alkyl group, "side chain."

HALOGEN DERIVATIVES OF BENZENE.

When a current of chlorin is passed into benzene at ordinary temperature, *monochlorbenzene*, $\text{C}_6\text{H}_5\text{Cl}$, is formed. It can also be produced from phenol by acting with phosphorus chlorid upon it; thus:



Description.—It is a colorless liquid, boiling at 136° . Through the continued action of chlorin at ordinary temperature upon this, especially in presence of a trace of iodine, *hexachlorbenzene*, C_6Cl_6 , is produced. When chlorin acts upon benzene at the temperature of the boiling-point, *benzene hexachlorid* is formed; this substance has the formula $\text{C}_6\text{H}_6\text{Cl}_6$. *Benzene hexachlorid* is a colorless, crystalline body, melting

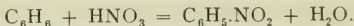
at 157°C. , and when heated decomposes into *trichlorobenzene*, $\text{C}_6\text{H}_3\text{Cl}_3$, splitting off hydrochloric acid:



Benzene hexabromid is similarly prepared by action of bromin.

NITRO-DERIVATIVES OF BENZENE.

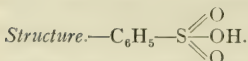
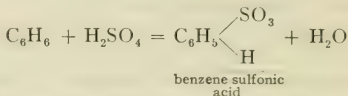
When benzene is slowly acted upon by nitric acid gradually added, *nitrobenzene*, $\text{C}_6\text{H}_5\text{NO}_2$, is formed. This product is washed with water, dried over calcium chlorid, and redistilled. It is a yellowish, oily liquid, boiling at 205°C. , and possessing a strong odor of the oil of bitter almonds. It is poisonous, and known under the synonyms of *oil of mirrbane* and "*artificial oil of bitter almonds.*" This latter term is especially *dangerous* in that it may be confounded with *benzaldehyd*. Reaction:



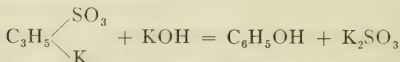
Dinitrobenzenes.—When benzene is boiled with fuming nitric acid, two hydrogen atoms are substituted and *dinitrobenzene*, $\text{C}_6\text{H}_4(\text{NO}_2)_2$, is formed. The dinitrobenzenes exist in three modifications, which may be distinguished by their melting-points, crystalline forms, etc.

Meta-DINITROBENZENE is best obtained by heating nitrobenzene for half an hour with a mixture of nitric and sulfuric acids. The product is poured into cold water, the precipitate washed, dried and crystallized from alcohol. Pale yellow crystals, melting at 90° , and soluble in organic solvents.

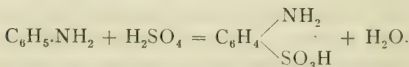
Preparation.—By treating the hydrocarbons with sulfuric acid:



When sulfonic acids are fused with potassium hydroxid, the hydroxyl replaces the sulfonic group and phenol is formed:



When anilin, $\text{C}_6\text{H}_5\cdot\text{NH}_2$, is treated with sulfuric acid, *sulfanilic acid* is formed, $\text{C}_6\text{H}_4 \begin{array}{l} \text{NH}_2 \\ \text{SO}_3\text{H} \end{array}$, called *para*-sulfonic acid:

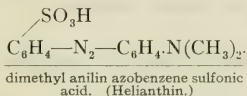


Sulfanilic acid is sparingly soluble in cold water; more soluble in hot water. It crystallizes in plates. When treated with nitrous acid, it yields *diazobenzene*

sulfonic acid, $\text{C}_6\text{H}_4 \begin{array}{l} \text{N}_2\cdot\text{OH} \\ \text{SO}_3\text{H} \end{array}$; this heated with di-

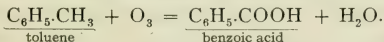
methyl-anilin gives **HELIANTHIN**, *tropaeolin D*,

methyl-orange, "Poirrier's orange," a valuable *indicator* in analytic chemistry:




TOLUENE AND ITS DERIVATIVES.

Toluene, $\text{C}_6\text{H}_5\cdot\text{CH}_3$, also called toluol, was so named from "tolu-balsam," from which it was first obtained by distillation (Pelletier, 1832). Toluene, phenyl-methane, is a light, mobile, oily liquid, insoluble in water, boiling at 110° , but otherwise resembling benzene. It occurs in coal-tar and balsam of tolu oil; it can be prepared by *Fittig's reaction*. When subjected to oxidation, only the methyl (side-chain) group becomes oxidized, giving rise to *benzoic acid*:



The synthesis of toluene from benzene clearly indi-

cates its structure to be . Toluene is some-

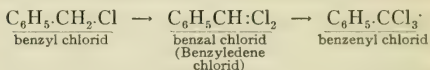
times considered as a methane, in which one hydro-
 CH_3
 gen was replaced by the phenyl group; thus, $\begin{array}{c} | \\ \text{C}_6\text{H}_5. \end{array} =$

phenyl-methane.

The term *phenyl* is applied to the monovalent radical C_6H_5' of benzene, and the "*aryl*" replaces *alkyl* among the aromatic radicals.

DERIVATIVES OF TOLUENE.

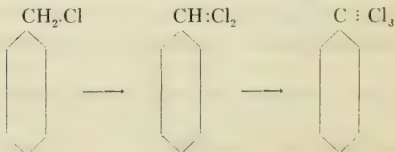
CHLORIN DERIVATIVES.—Like benzene, toluene forms substitution-products with chlorin and bromin. The substitution may take place either in the side chain or in the nucleus. By *boiling* toluene and passing chlorin into it, substitution in the *side chain* will occur; the following products being successively produced:



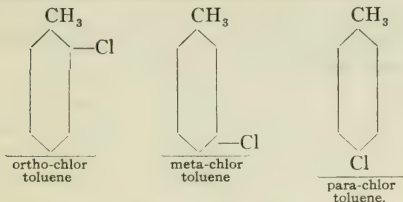
The first compound contains the *monovalent radical benzyl*, $C_6H_5 \cdot CH_2'$; the second, a *divalent radical benzal*, $C_6H_5 \cdot CH''$, and the third, a *trivalent radical benzenyl*, $C_6H_5 \cdot C'''$.

If chlorin is passed into *cold* toluene, substitution takes place in the *nucleus*, and mono-, di- and trichlor- toluenes are produced.

Examples of substitution in the side chain:



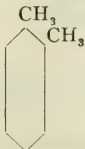
Examples of substitution in the nucleus:



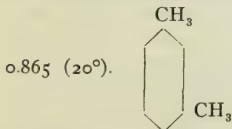
XYLENES AND THEIR DERIVATIVES.

XYLENE exists in three modifications:

Ortho-**XYLENE** may be prepared by heating methyl iodid with *ortho*- bromtoluene in presence of metallic sodium. It is a colorless liquid, boiling at 142° , and having a specific gravity of 0.876 (20°).



Meta-**XYLENE** is prepared by heating *meta*- iodo-toluene with methyl iodid in presence of metallic sodium. *Meta*-xylene boils at 139° ; specific gravity,



Para-**XYLENE** can be made by methods similar

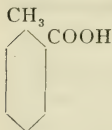
with the above or by distilling camphor with zinc chlorid.

Para-xylene boils at 137° and has a specific gravity of 0.863 (20°).



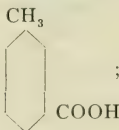
Properties.—When oxidized, the xylenes yield the dibasic ortho-, meta- and paraphthalic acids, and by substitution yield derivatives similar to toluene.

The oxidation occurs in two stages; thus, first, the *three toluic acids* are produced:



o-toluic acid

;



m-toluic acid

;



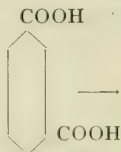
p-toluic acid.

on further oxidation, each of these yields a corresponding dibasic acid:



phthalic acid
melting-point
 213° .

→



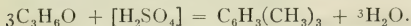
isophthalic acid
melting-point
 300° .

→

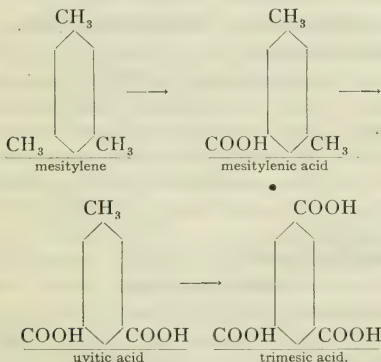


terephthalic acid
sublimes with-
out melting

Mesitylene, $C_6H_3(CH_3)_3$ (1, 3, 5), is produced by the action of strong sulfuric acid upon acetone:

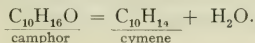


Chemically, *trimethyl benzene* can be produced from the xylenes by Fittig's reaction. It boils at $160^\circ C$ and has a pleasant odor. When oxidized, mesitylene yields a series of acids:

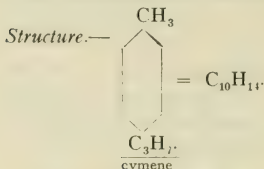


Cymene, $C_6H_4.CH_3.C_3H_7$, *para-methylpropyl-benzene* occurs naturally in the essential oils, like oil of thyme, etc., and can be produced artificially by the action of dehydrating agents upon these.

Thus, when camphor is distilled with phosphorus pentoxid, cymene is produced:



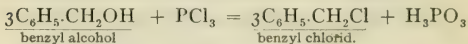
Cymene possesses a pleasant odor, boils at 175° and has the specific gravity, 0.856 (20°)



DERIVATIVES OF THE HOMOLOGUES.

CHLORTOLUENE, *toluyl chlorid*, $\text{C}_6\text{H}_4\text{Cl}.\text{CH}_3$ occurs in three modifications like all the disubstituted benzenes. When *cold* toluene is acted upon with chlorin, a mixture of the *ortho*- and *para*- varieties is produced. By treating the corresponding cresols, any of the three modifications may be produced. The *cresols* are *hydroxytoluenes*. Chlortoluenes boil at about 156°C .

BENZYL CHLORID, $\text{C}_6\text{H}_5.\text{CH}_2\text{Cl}$, is prepared by passing chlorin into *boiling* toluene, also by acting with phosphorus chlorid upon benzyl alcohol:

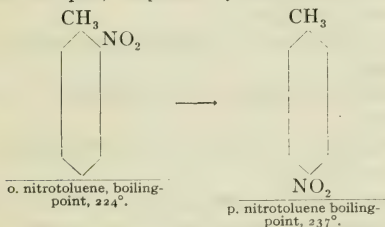


[Benzyl alcohol is produced by replacing one hydrogen atom of the *side chain* in toluene with a hydroxyl.]

Benzylchlorid is insoluble in water, but soluble in organic solvents, it possesses a penetrating odor and boils at 176°C . With water it hydrolyzes into benzyl alcohol and hydrochloric acid; with nitric acid it forms nitro derivatives.

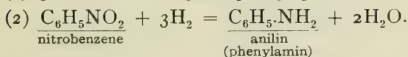
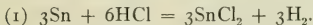
BENZALCHLORID, $C_6H_5.CHCl_2$, is obtained by the prolonged boiling of toluene and chlorin. It is a colorless, oily liquid, boiling at 206° .

NITROTOLUENES.—When toluene is treated with strong nitric acid, substitution always occurs in the phenyl. The chief nitrotoluene is the *para* with which a little *ortho* compound forms at the same time. These may be separated by fractional distillation since they have different boiling-points, besides, *ortho* is a liquid, the *para* a crystalline solid:



AROMATIC AMINS.

When a nitro compound is treated with nascent hydrogen, an *aromatic amin* and water are produced. Thus, if nitrobenzene, $C_6H_5NO_2$, is treated with a mixture of metallic tin and hydrochloric acid, hydrogen is generated and the nitro group reduced:



ANILIN, amidobenzene, phenylamin, $C_6H_5NH_2$, is prepared as above. It was first obtained by

distilling indigo (Portuguese for indigo is *anil*). Anilin is found in coal-tar, also in Dippel's oil" (bone oil). It is the simplest member of the group of aromatic amines and occurs as a colorless oil *when pure*—more frequently of a yellowish or brownish color, possessing a characteristic odor, sparingly soluble in water, but readily in other organic solvents. It boils at 183° , is poisonous, and with the acids it forms additive compounds. Chemically, it is a *substituted ammonia*.

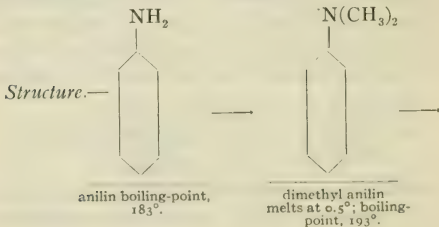
Salts with the acids:

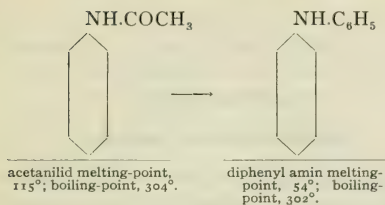
$C_6H_5.NH_2 + HCl = C_6H_5NH_2.HCl$ = anilin hydrochlorid.

$C_6H_5.NH_2 + HNO_3 = C_6H_5NH_2.HNO_3$ = anilin nitrate.

$2C_6H_5.NH_2 + H_2SO_4 = (C_6H_5.NH_2)_2.H_2SO_4$ = anilin sulfate.

Anilin salt of the trade is the anilin *chlorid*. These salts treated with alkali hydroxids are resolved back into anilin, water and a corresponding salt; thus:

$$\underbrace{C_6H_5.NH_2.HCl}_{\text{anilin chlorid}} + KOH = \underbrace{C_6H_5NH_2}_{\text{anilin}} + H_2O + KCl.$$


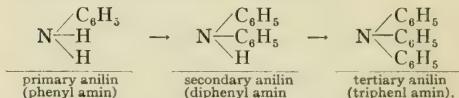


CHAPTER XXXIV.

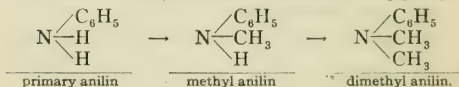
DERIVATIVES OF ANILIN.

ANILIN is much more reactive with ordinary reagents than either benzene or its halid or nitro-derivatives.

ALKYL ANILINS are compounds corresponding in constitution to the secondary aliphatic amins. It should be remembered that we can have *primary*, *secondary* and *tertiary aromatic amins*, just as we have the aliphatic substituted ammonias:

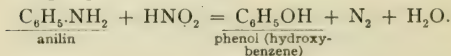


Or we have an alkyl as one of the substituting groups:

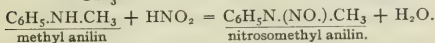
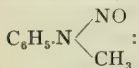


Identification of Aromatic Amino Compounds.—They may be identified much like the aliphatic amins.

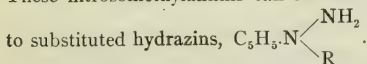
(1) *Primary amins with nitrous acid*, upon warming, effervesce, the NH_2 group is replaced by an OH group:



(2) *Secondary amins with nitrous acid* give *nitrosamin*, a yellow substance, insoluble in water. Thus, methyl anilin gives a *nitrosomethylanilin*,

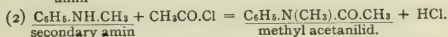
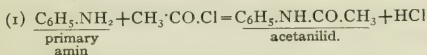


These nitrosomethylanilins can further be reduced

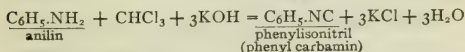


(3) *Tertiary amins with nitrous acid* give a deep red solution, from which yellow crystals will separate; thus, in the case of dimethylanilin, *nitrosodimethylanilin* is formed.

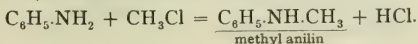
With *acetyl chlorid* or *acetic anhydrid*, *primary* and *secondary aromatic amins* form *acetyl* derivatives; the *tertiary amins* do not; thus:



The primary amins, furthermore, with alcoholic potash and chloroform give the *carbamin* (isonitрил) reaction:



METHYL ANILIN, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}_3$, is prepared by acting with methyl chlorid on anilin:



It occurs as a strongly basic liquid, boiling at 90°C .

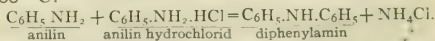
DIMETHYL ANILIN, $\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_3)_2$, is also produced in the previous reaction. It occurs as a strongly basic, oily liquid, boiling at 190°C .

TOLUIDINS exist in three modifications, of

which the *para-toluidin*, $\text{C}_6\text{H}_4 \begin{matrix} \nearrow \text{NH}_2 \\ \searrow \text{CH}_3 \end{matrix}$, prepared

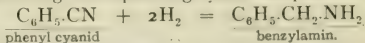
from *para*-nitrotoluene, is the best known. *Toluidins* are *amido-toluenes* and bear the same relation to toluene as anilin does to benzene. The toluidins resemble anilins in properties. When oxidized, toluidin yields *rosanilin*, the parent substance of many *anilin dyes*.

DIPHENYLAMIN, $(\text{C}_6\text{H}_5)_2\cdot\text{NH}$, is formed from anilin by the introduction of a second phenyl, C_6H_5 , group in the side chain. This is usually accomplished by heating anilin with anilin chlorid at 200°C :



Diphenylamin crystallizes in white lamina from ligroin, and has a melting-point of 54° , boiling-point of 302°C . It forms salts with strong acids, which are decomposed by water.

BENZYLAMIN, $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{NH}_2$, is isomeric with toluidin, and can be prepared, like the alkylamins, by reducing corresponding cyano-compounds:



Benzylamin resembles closely the alkylamins in

their properties. It occurs as a mobile, colorless liquid, soluble in water, with a pungent odor and a boiling-point of 185° C. Specific gravity, 0.983 (19° C).

ACETANILID, acetanilidum $C_6H_5NH(CHCO)$, antifebrin, phenylacetamid. A monacetyl derivative of anilin. Made by the condensation of anilin and glacial acetic acid. A crystalline white powder, soluble in 180 parts water, in 25 parts alcohol, 18 parts ether and 5 parts chloroform. Melting-point 113° C. Used as antipyretic, analgesic, antirheumatic, sedative, antiseptic. Used in fevers, headache, neuralgia. Externally, as antiseptic, instead of iodoform. Also as preservative of hypodermic solutions. Incompatible with nitrous ether, bromids, iodids, chloral hydrate, phenol, resorcin and thymol (with these it liquefies).

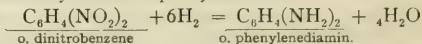
Acetanilid should be carefully tested before using in pharmacy. It *should give the phenylisocyanid test*, which distinguishes it from *methyacetanilid* and *antipyrin*. A cold, saturated solution of acetanilid should *not affect ferric chlorid* test solution, showing the *absence of anilin salts*.

XYLIDINS are *amido-xylenes* and bear the same relation to the three xylenes that anilin bears to benzene. They are difficult of preparation in the pure condition. p. xylidin is made by reducing p. nitro-xylol with nascent hydrogen.

DIAMINS.—Besides the *monamins*, like anilin,

$C_6H_5.NH_2$, there is a class of *diamins*, C_6H_4 $\begin{matrix} \nearrow NH_2 \\ \searrow NH_2 \end{matrix}$.

Preparation.—The diamins are prepared by reducing the dinitro-benzenes. Thus, *orthodinitrobenzene* yields *orthophenylene diamin*:



The *meta*- and *para*- varieties are similarly prepared. *Orthophenylenediamin* melts at 102°C . *Meta*-phenylenediamin melts at 63°C ., and the *para*- compound melts at 147°C .

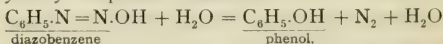
Metaphenylenediamin, with traces of nitrous acid salts, gives intense brown-colored diazo colors, and hence it is valued in water analysis for the *detection of nitrites*.

THE DIAZO COMPOUNDS.

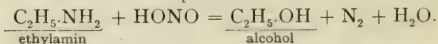
When a primary aromatic amin is treated with *cold nitrous acid*, *diazobenzene* is produced:



This, when warmed, is decomposed, and a *hydroxy* compound formed:



The production of this intermediate diazo compound distinguishes the aromatic from the aliphatic amins and also from those aromatic amins containing the— NH_2 group in the side chain; these react without the intermediate product:



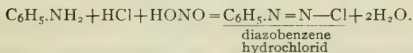
THE DIAZO COMPOUNDS may be said to *contain two nitrogen atoms for each phenyl group* (Gries, 1858).

DIAZOBENZENE NITRATE, $C_6H_5-N=N-NO_3$, also called *benzene diazonium nitrate* (Gries, 1866), occurs in silky crystals, and is *exceedingly explosive*. It is produced by acting with nitrous acid upon anilin nitrate at a very low temperature. It is poisonous, and decomposes at ordinary temperatures. A compound allied to the above is *diazobenzene-butyrate*, $C_6H_5-N=N-C_4H_6O_2$, called *tyrotoxin*; found in fermented ice cream, and known as "ice cream poison."

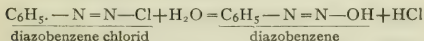
The cases of poisoning with tyrotoxin are very common in the summer time.

DIAZOBENZENE, $C_6H_5-N=N-OH$, is obtained by mixing two very cold solutions, one of anilin in hydrochloric acid, the other of amyl nitrite in alcohol. A crystalline, colorless body separates out, and speedily acquires a brownish color on exposure.

Reaction:



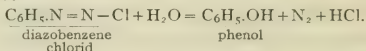
The *diazobenzene sulfate* may be obtained in the same way. By the addition of potassium hydroxid, a *potassium salt* is obtained which can be *decomposed* with *acetic acid*, giving the very unstable diazobenzene:



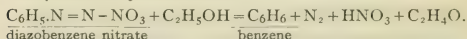
This is an unstable, colorless, explosive salt. Its unstable character is taken advantage of in the preparation of other classes of aromatic compounds.

REACTIONS OF THE DIAZO COMPOUNDS.

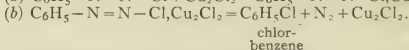
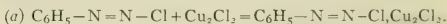
(1) When a diazo compound is *boiled* with *water*, it becomes brown, evolves nitrogen and *forms a phenol*:



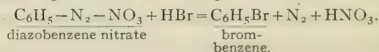
(2) When a diazo-compound is *dissolved* in *alcohol* and *heated* for some time, it evolves nitrogen and *forms a hydrocarbon*:



(3) When a diazo compound, dissolved in cold water, is mixed *with cuprous chlorid*, *chlorbenzene* is *formed*. The copper salt acts as a catalytic. An addition compound of the copper and diazo salt first forms, and this on warming regenerates the cuprous chlorid:



(4) When a diazo compound is heated with *hydrobromic*, *hydrochloric* or *hydriodic acids*, a corresponding benzene halid is produced:

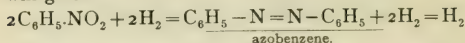


REDUCTION OF DIAZO COMPOUNDS.

When diazobenzene hydrochlorid is reduced by stannous chlorid in hydrochloric acid, it is converted into *phenyl-hydrazin hydrochlorid*.

PHENYLHYDRAZIN, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2$, may be said to be derived of *hydrazin*, $\text{NH}_2\cdot\text{NH}_2$

benzene, dissolved in a solution of sodium hydroxid, will give:



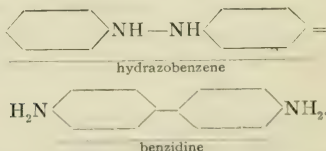
As stated under Diazobenzenes, they are compounds containing *two nitrogens for each phenyl*; the azo compounds contain *two nitrogens to two phenyl groups*.

AZOBENZENE, $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$, crystallizes in red tablets, melting at 94°C ., and subliming at 293°C . By further reduction, *hydrazobenzene*, $\text{C}_6\text{H}_5\text{NH} - \text{NH} - \text{C}_6\text{H}_5$, is produced.

The higher and more complex azo compounds are all highly colored, and much valued as dyes.

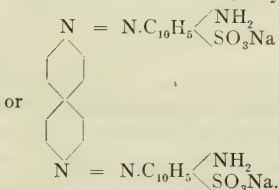
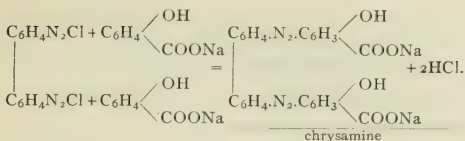
Hydrazobenzene oxidizes in the air turning orange color and forming azobenzene. By boiling with strong hydrochloric acid, *amino azobenzene* is formed.

BENZIDINE, aminoazobenzene, diaminodiphenyl, is a strong base, $\text{C}_{12}\text{H}_8(\text{NH}_2)_2$, a very important substance in the preparation of *benzidine dyes*:

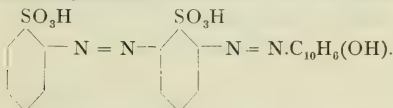


Of the important benzidine dyes, the following may be mentioned:

CHRYSAMIN, made by acting with sodium salicylate upon diphenyltetrazochlorid:



BIEBRICH SCARLET =

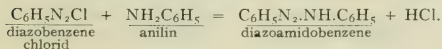


The benzidine dyes can be used in dyeing cotton without a mordant.

THE DIAZO-AMIDO COMPOUNDS.

This series of compounds is formed by *adding an amido to a diazo compound*. These compounds, upon standing, are transformed into **AZO-AMIDO COMPOUNDS**.

DIAZOAMIDOBENZENE is obtained as follows:

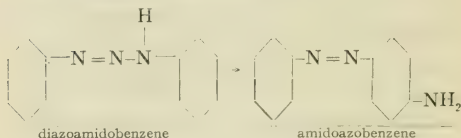


This compound occurs in golden-yellow prisms which, when heated with anilin, yield:

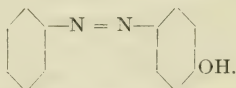
AMIDOAZOBENZENE,



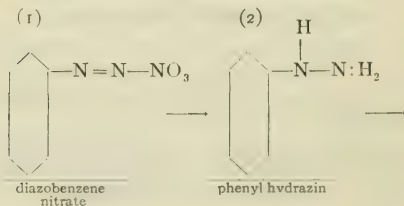
Structures of the two:

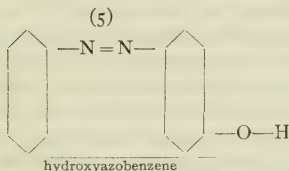
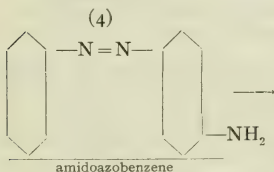
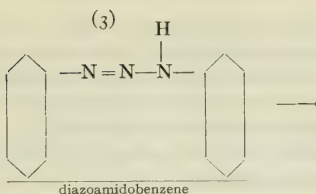


THE HYDROXYAZO-BENZENES are formed from phenol and a diazo compound. Like the *amido-azo benzene*, they form valuable dyes, of which those derived from para-amidosulfonic acid—are mostly valued, in that they dye silks and wool without a mordant. Structure:



The *relationship of the nitro compounds* is best shown by the following *structural formulas*:





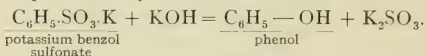
HYDROXY BENZENES.

There are three classes of hydroxy benzenes: those containing *one hydroxyl* —OH group known as *phenols*, those containing *two hydroxyls*, known as *diatomic or dihydroxyphenols*, and with *three hydroxyls*, the *triatomic phenols*. The *monatomic phenols* have *no isomers*, but the *diatomic phenols* each have *three isomers*.

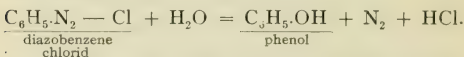
There are two kinds of hydroxyderivatives of

the aromatic hydrocarbons: those in which the hydroxyl group is substituted for the hydrogen of the nucleus and those in which the substitution takes place *in the side chain*. The first kind are known as *phenols*, the last as *aromatic alcohols*.

Preparation.—(1) By fusion of sulfonic acids with potassium hydroxid:



(2) By prolonged boiling of diazobenzene chlorid with water:



Properties.—The phenols contain the tertiary alcohol group C—OH , and therefore appear to be allied to the tertiary alcohols; and in reality they are acted upon similarly by the oxidizing agents. Like alcohols, the phenols form ethers and esters; and, as stated above, they may be monacid ($\text{C}_6\text{H}_5\cdot\text{OH}$), diacid ($\text{C}_6\text{H}_4(\text{OH})_2$), or triacid ($\text{C}_6\text{H}_3(\text{OH})_3$).

Phenols and the aromatic alcohols are isomeric, but possess entirely different properties.

PHENOL, $\text{C}_6\text{H}_5\text{OH}$, phenol, phenic acid, phenyl alcohol, phenyl hydrate (acidum carbolicum U. S. P. '90). Chemically, it is not an acid, but a phenol or hydroxy benzene, hence the change in pharmacopœial name. Purity, 96%. Phenol resembles creasote in its odor and caustic properties, but differs in chemical composition in being a solid at ordinary temperatures. Melting-point, 40° . It is soluble

in 9.6 parts water (creasote in 140 parts water). Boiling-point, 100° C. Insoluble in benzin, and coagulates collodion when mixed with it.

Phenol liquefactum, liquefied phenol. Strength, 86.4% of phenol, 13.6% of water. Prepared by melting phenol in an unstoppered bottle on a water-bath and mixing it with 10% of its weight of distilled water. By using alcohol instead of water, corking the bottle and placing "upside down," solution may be effected without heat. Dose, 1 gr., largely diluted. It is a caustic and deadly poison. Alcohol prevents its caustic effect, and should be first administered, followed by large doses of magnesium sulfate in solution, which forms a harmless sulfocarbolate of magnesium. Preparations: Unguentum phenolis (3%); glyceritum (liquefied phenol, 20 %). Used as a disinfectant and antiseptic dressing. Carbolic *lotion* is prepared by dissolving one part of the acid in 30 parts hot water (carbolyzed water).

Note.—Observe that the *solution* of phenol is of 5% strength, while *liquefied* phenol is 86.4%.

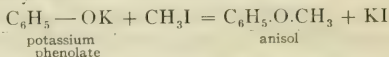
Tests.—With *ferric chlorid*, dilute solutions of phenol are *colored violet*.

With bromin water a precipitate of tribromphenol is produced. This is known as *bromal*, $C_6H_2Br_3OH$, upon the formation of which the phenol assay method depends.

PHENOL ETHERS.—There are many valuable ethers and esters of phenol, many of which replace the natural odors of the flowers.

PHENYLMETHYL ETHER, $C_6H_5.O.CH_3$, is called

anisol. It can be obtained from anisic acid (methoxybenzoic acid) by boiling with barium hydroxid, or by synthesis from potassium phenolate with an alkyl halid:



ETHYLPHENYL ETHER, or *phenetol*, is $\text{C}_6\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$, and can be produced by the above method, using an ethyl halid.

DIPHENYL ETHER, $\text{C}_6\text{H}_5.\text{O}.\text{C}_6\text{H}_5$, resembles the ethyl ether. Among the esters we may mention:

PHENYL ACETATE, $\text{C}_6\text{H}_5.\text{O}.\text{CO}.\text{CH}_3$, can be obtained by treating phenol with acetyl chlorid.

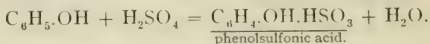
OTHER DERIVATIVES OF PHENOL.

THE PHENOL SULFONIC ACIDS.—When phenol is dissolved in concentrated sulfuric acid, upon warming, a mixture of *ortho*- and *para*-sulfonic acids is formed. These are colorless, deliquescent, crystalline bodies, which, when fused with potassium hydroxid, *yield corresponding diatomic phenols*.

Phenolsulfonic acids are variously known as *sulfo-carbolic* or *sozolic acids*, also as *aseptol*, and have

the formula $\begin{array}{c} \diagup \text{C}_6\text{H}_5\text{OH} \\ \text{SO}_2 \\ \diagdown \text{OH} \end{array}$

Preparation.—By dissolving phenol in strong sulfuric acid:



Used as an antiseptic wash in 10% aqueous solutions.

SODIUM PHENOLSULFONATE, sodii phenol-sulfonas (sulfocarbolas, '90), sodium sulfocarbolate, $\text{NaSO}_3\text{—C}_6\text{H}_4\cdot\text{OH}$, is prepared by acting with phenosulfonic acid on sodium carbonate; a white, crystalline, soluble salt.

SODIUM ICHTHYO-SULFONIC ACID, ichthyol, also *ammonium ichthyo sulfonate*, obtained by destructive distillation of bituminous shale found in Tyrolean Mountains. Undoubtedly obtained from fossilized aquatic animals by dry distillation. A dark oily distillate is obtained which, treated with an excess of sulfuric acid, yields ichthyolsulfonic acid. This latter product is purified and neutralized with ammonia or sodium hydroxid, yielding, correspondingly, the ammonium or sodium salt. The substance contains about 10% of sulfur. It is soluble in water, glycerin and the oils, also in a mixture of alcohol and ether. Used in skin and rheumatic affections, also in lung affections, exhibited in keratin-coated capsules. *Formula*, $\text{C}_{28}\text{H}_{36}\text{S}_3\text{O}_6$.

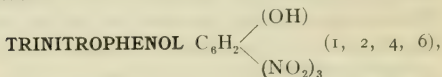
THE NITRO PHENOLS, $\text{C}_6\text{H}_4 \begin{matrix} \nearrow \text{NO}_2 \\ \searrow \text{OH} \end{matrix}$. When

dilute nitric acid acts upon phenol, *ortho*- and *para*-mononitro phenols are yielded. These are separated by steam distillation, the *orthonitrophenol* being volatilized.

ORTHO-NITROPHENOL is slightly soluble in water, readily in the organic solvents. It occurs in canary-yellow crystals, melting at 45°C .

PARA-NITROPHENOL occurs in colorless needles,

melting at 114° C.; also soluble in water to a small extent.

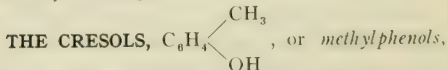


picric or *carbazotic acid*, is formed very easily when strong nitric acid acts upon phenol. This is best done in the presence of sulfuric acid. This acid also results from the action of strong nitric acid on various substances such as wool, silk, resin, and indeed, the yellow stains upon the hands produced by strong nitric acid are due to picric acid.

Picric acid occurs in brilliant yellow crystals, melting at 123° C.; soluble in hot water, and re-depositing as the solution cools. It explodes under percussion and is extensively used for this purpose under the name *lyddite*. *Ammonium picrate*, $C_6H_2(NO_2)_3 \cdot O.NH_4$; is also used in explosives.

Picric acid possesses acidic properties and readily forms salts. It is a good yellow dye for wool and silk, but the color is affected by light. It will *not* dye cotton, and thereby forms a reliable test for its detection in mixed goods.

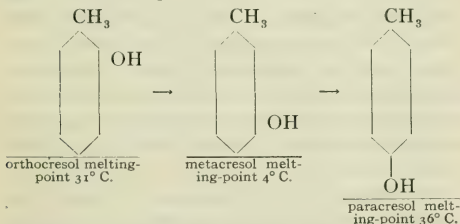
PHENYL MERCAPTAN, $C_6H_5.SH$, *phenyl hydro-sulfid*, *thiophenol*, bears the same relation to phenol that mercaptan does to alcohol. It can be prepared by reducing benzene-sulfonic acid.



cresylic acids, *hydroxy toluols*. There are three

isomeric cresols, all found in pine- and coal-tars; they are similar to phenol. To obtain pure cresols, it is best to prepare these from the three toluidins.

CRESOL, C_7H_7OH (Duclos, 1859), formerly known as cresylic acid, a mixture of three isomeric cresols is obtained from coal-tar and separated from phenol by fractional distillation. It is a refractive liquid of a strong, phenol-like odor, colorless, but becoming brown on exposure, soluble in 60 parts water and all other solvents. Used as disinfectant and deodorant. One to 5% solutions are more certain antiseptics than phenol minus its poisonous properties. Creolin, lysol, are preparations similar to *Liquor cresolis compositus*, a 50% solution of cresol in soft soap.



CREASOTE is a mixture of phenols, cresols and guaiacol, obtained from wood (*fagus silvatica*), tar. There is also coal-tar creasote in commerce, which consists largely of phenol.

CREASOTUM.—A mixture of several substances belonging to the class known as phenols. It is obtained by distilling wood-tar, preferably that from

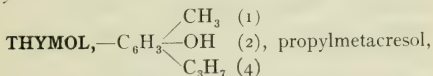
beechwood. Boiling-point above $200^{\circ}\text{C}.$; consisting chiefly of guaiacol ($\text{C}_7\text{H}_8\text{O}_2$) and cresol ($\text{C}_8\text{H}_{10}\text{O}_2$). The distillate from tar separates into two layers; the heavier one is freed from impurities by treatment alternately with KOH and H_2SO_4 , and the portion boiling between 200° and $220^{\circ}\text{C}.$ is separated by fractional distillation. An almost colorless, oily liquid, of a penetrating, smoky odor and a burning, caustic taste, darkening on age; gelatinizes but does not solidify at the freezing-point (difference from phenol). It is inflammable, burning with a smoky flame. It coagulates the albumin of the skin, producing a white stain. It is neutral. Specific gravity, 1.07. Soluble in 140 parts water (phenol in 19.6 parts water). It is soluble in benzin and does not coagulate collodion (difference from phenol). It is also soluble in alcohol, ether, chloroform, fixed and volatile oils. Used to deaden pain and preserve tissue, as an application in toothache; internally to allay nausea; in consumption and lung diseases. Preparation: Aqua creasoti (a saturated solution).

GUAIACOL, $\text{C}_7\text{H}_8\text{O}_2$. Guaiacol, the chief constituent of creasote (85%), is obtained by purification and fractional distillation. Synthetically, by methylation of catechol. A colorless, refractive liquid, of an agreeable, aromatic odor; specific gravity, 1.14; or a crystalline solid melting at $28.5^{\circ}\text{C}.$ Soluble in 53 parts water, in alcohol and ether in all proportions, and in 1 part glycerin. Used as substitute for creasote in tuberculosis, in elixirs, syrups oils,

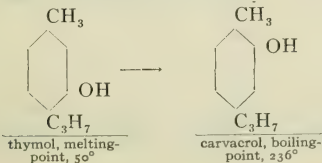
emulsions and in capsules. Chemically, it is monomethyl pyrocatechol, $C_6H_4 \begin{matrix} \diagup O-CH_3 \\ \diagdown OH \end{matrix}$.

GUAIACOL CARBONATE, guaiacolis carbonas, $(C_7H_7O)_2CO_3$. Obtained by the action of carbonyl chlorid on sodium guaiacolate. An almost tasteless, odorless, white, crystalline powder, insoluble in water; soluble in 48 parts alcohol; in 1.5 parts chloroform; slightly in ether. Used as guaiacol in tuberculosis in powder form. Chemically, it is di-monomethyl pyrocatechol carbonate $\left(\begin{matrix} C_6H_4 \cdot CH_3 \cdot O \\ C_6H_4 \cdot CH_3 \cdot O \end{matrix} \right) > CO_3$.

Among the higher monatomic phenols, we have *thymol* and *carvacrol*.



is a phenol occurring together with cymene in the oil of thyme. It can be synthetically prepared from nitrocuminic aldehyd, $C_6H_3-CHO-NO_2-C_3H_7$ (1, 3, 4). Thymol forms large monoclinic crystals, melting at 50° , its odor reminds one of thyme, it is one of the two possible hydroxy derivatives of cymene, the other being carvacrol, which has also been obtained from the oil of caraway:



AMIDOPHENOLS, $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown NH_2 \end{smallmatrix}$, are produced

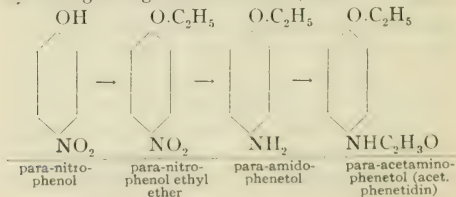
by reducing the corresponding nitrophenols with hydrogen. They occur as colorless crystalline substances, basic in character. *Meta-amidophenol* forms the basis of some of the *rhodamin dyes*.

Para-amidophenol is a solid, melting at 184° , and yielding an ethyl ether paraphenetidin,

$C_6H_4 \begin{smallmatrix} \diagup OC_2H_5 \\ \diagdown NH_2 \end{smallmatrix}$, this is converted by glacial acetic acid into an acetyl derivative *phenacetin*.

PHENACETIN (acetphenetidinum), $C_6H_4.NH.C_2H_5O.(C_2H_5O)$. A phenol derivative made by acetalizing para-amidophenol. Chemically, para-aceticphenetidid. White, crystalline scales or powder, odorless, tasteless. Soluble in 925 parts water, 12 parts alcohol, also ether and chloroform. Used as analgesic and antipyretic in powders or capsules. It melts at $134^\circ C.$, should not give precipitate with bromin water (acetanilid).

Preparation.—From para-nitrophenol, by converting it into nitrophenylethyl ether, this reduced with hydrogen to form para-amidophenol, this acetylated by boiling with glacial acetic acid; thus:

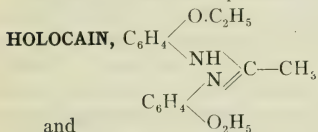


If, instead of acetic acid, lactic acid be employed in the last reaction:

LACTOPHENIN, $C_6H_4 \begin{smallmatrix} \diagup NH.C_3H_5O_2 \\ \diagdown O.C_2H_5 \end{smallmatrix}$, is produced.

Both are used as antipyretics.

Two other derivatives of para-amido—phenol are:

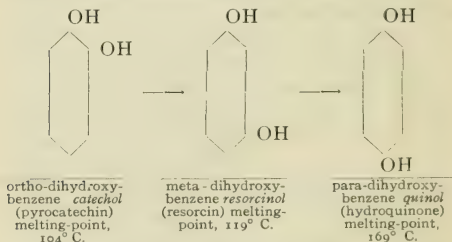


PHENOCOLL, $C_6H_4 \begin{smallmatrix} \diagup O.C_2H_5 \\ \diagdown NH.CO.CH_2.NH_2 \end{smallmatrix}$ = amido-acetic acid derivative.

CHAPTER XXXV.

DIATOMIC PHENOLS.

THERE are three isomeric diatomic (diacid) phenols. They are produced by fusing together the disulfonic acids with potassium hydroxid. They occur in horses' urine (pyrocatechin), and in human urine (hydroquinon) after administration of phenol; resorcinol is obtained by melting galbanum, asafetida and other resins:



CATECHOL, pyrocatechin, $C_6H_4(OH)_2$, (1.2), occurs in nature in cutch, from which it derived its name, in kino, and obtained by the fusion of many gums with the alkalis.

It is a colorless crystalline solid, soluble in water and in other solvents. Its solutions in alkali hydroxids absorb oxygen from the air and rapidly become brown.

With ferric chlorid its solutions are colored green—

this being characteristic of all the ortho-dihydroxy phenols.


When catechol is treated with methyl iodid, mono-methyl ether of catechol, *guaiacol*, $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown OCH_3 \end{smallmatrix}$, is produced.

RESORCINOL (resorcinum), $C_6H_4(OH)_2$, (1.3), resorcin, a diatomic phenol (metadihydroxy benzene). Obtained by action of alkalis on metabenzene disulfonates. Faintly reddish crystals; very soluble in alcohol and water. Melting-point, 110° to 111° C. Used as antiseptic, antiseborrheic in solutions, ointments, etc. Incompatible with ferric chlorid (violet color); with hypochlorite solutions (violet to yellow), with spirit of nitrous ether (dark red); on trituration, it liquefies or softens with phenol, menthol, camphor, chloral hydrate, acetanilid, anti-pyrin, etc.

With phthalic anhydrid, when heated, resorcin forms a brown substance, which is soluble in caustic alkalis. The alkali solution of the body added to water produces brilliant green fluorescence, and hence the name of—

FLUORESC EIN, $C_{20}H_{12}O_5$, *resorcin-phthalein*, has

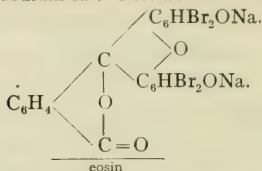
the structure $C \begin{smallmatrix} \diagup C_6H_3(OH)_2 \\ \diagdown C_6H_3(OH)_2 \\ \diagdown C_6H_4C=O \end{smallmatrix}$, and is mostly used in



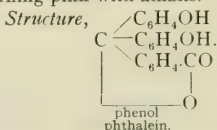
the making of—

EOSIN or tetrabromfluorescein pink dyes. When fluorescein is acted upon by bromin in acetic acid

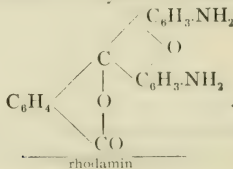
solution, eosins are produced. The ordinary eosin dye is the sodium salt of tetrabromfluorescein:



PHENOLPHTHALEIN is obtained by heating one molecule of phthalic anhydrid with two molecules of phenol to 115°C . With the addition of strong sulfuric acid, phenolphthalein is formed. It occurs as a white, crystalline substance, melting at 251° ; slightly soluble in water, but soluble in alcohol. It constitutes a valuable indicator in volumetric analysis, turning pink with alkalis.

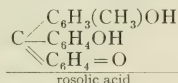
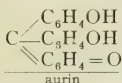


RHODAMINES constitute some of the best brilliant red dyes. They are obtained from meta-amidophenol and phthalic anhydrid. *Structure,*



AURIN is prepared by heating together phenol and oxalic acid in presence of strong sulfuric acid.

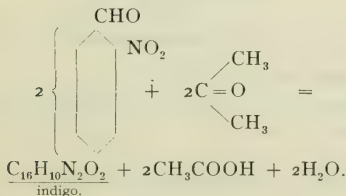
ROSOLIC ACID is prepared from a mixture of phenol, cresol and arsenic acid in presence of a dehydrating agent. Both the above dyes are structurally represented—



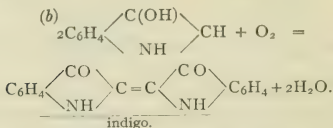
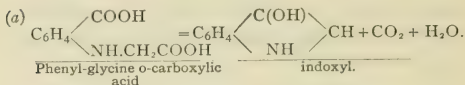
INDIGO, one of the most valuable blue dyes, is obtained from the leaves of the indigo plant (*indigofera tinctoria*), indigenous to India. Commercial indigo is not the pure substance, but a mixture of varying quantities of other coloring matters, as *indigo brown*, *indirubin*, etc. It can be purified by crystallizing it from anilin, and as such it is known as *indigotin* or “*pure indigo*.”

Indigo synthesis has taken up the chemist's attention for many years. It is now prepared synthetically by one of two following methods:

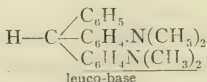
(1) From ortho-nitrobenzaldehyd and acetone with dilute sodium hydroxid solution:



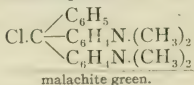
(2) From anthranilic and chloracetic acid forming phenyl-glycine o-carboxylic acid; the process consists of two steps:



MALACHITE GREEN, *benzaldehyd green*, is made by heating together benzaldehyd, dimethyl anilin and zinc chlorid. This forms the water-insoluble, colorless *leuco-base*,



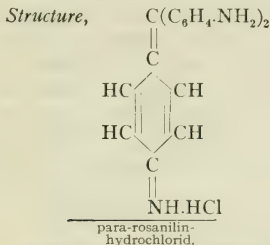
this, oxidized with lead peroxid and HCl, gives



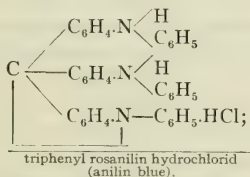
ROSANILIN, also called fuchsin and magenta, was originally obtained by heating anilin and para-toluidin with arsenic. It was one of the first dyes produced.

The product is *magenta arsenate*, which, on addi-

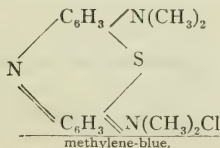
tion of sodium chlorid, is converted into the hydrochlorid.



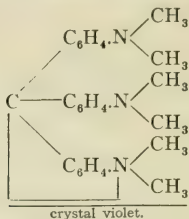
ANILIN BLUE is obtained from rosanilin by heating it with anilin and acetic acid. Each of the three amino groups loses one hydrogen atom which is replaced by a phenyl-group:



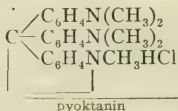
METHYLTHIONIN HYDROCHLORID is—



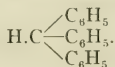
CRYSTAL VIOLET is the hexamethyl derivative of para-rosanilin. It has the structure



METHYL VIOLET has the structure

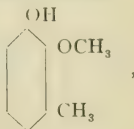


The above dyes, with the exception of indigo, may be said to be derivatives of *triphenylmethane*,



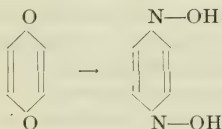
Many other important dyes are known, but of less interest to the pharmaceutical student than the above types.

CREOSOL, methyl dioxytoluene,



occurs in creasote.

QUINOL, $C_6H_4(OH)_2$, hydroquinon, hydroquinon is usually made by reducing *quinon* or by fusing paraiodophenol with potassium hydroxid. It occurs in leaflets or prisms melting at $169^\circ C$.; soluble in water. Its alkalin solutions absorb oxygen from the air. It is used for the above reason in photography as a reducing agent. By oxidizing hydroquinon *quinon* is produced, $C_6H_4O_2$; with two molecules of hydroxylamin it forms quinon-dioxime,



ORCINOL, *dihydroxytoluene*, $C_6H_3CH_3(OH)_2$, can be conveniently classed with the dihydroxyphenols. Orcinol is obtained from several varieties of lichens, artificially by melting chlortoluene sulfonic acid with potassium hydroxid. It occurs in colorless prisms which turn red on exposure, and with ferric chlorid, deep blue.

Orcinol treated with ammonia is converted into *orcein*, $C_{28}H_{24}N_2O_7$, which with alkalis gives a red dye. This is the chief use of orcin.

Orcin is closely related to *archil*, *litmus* and *cudbear*, three dye-stuffs, all prepared from the lichens by macerating them with urine which, when decomposed, yields ammonia, and this develops the coloring principles.

DYEING.

Having mentioned the important dyes, a discussion of dyeing should prove interesting and instructive.

It has been stated that a large part of the economic value of coal-tar products consists in the dyes made therefrom.

Thus, the important "Turkey-red" from madder, "indigo" from the indigo plant of India and "logwood black" from logwood, have all been replaced by the corresponding *alizarin* from anthracene, *indigo* from naphthalene and *nigrosin* from anilin.

Likewise the number of plant dyes are limited while the artificial dyes are almost numberless and constantly increasing in number.

DYES are frequently *classified* in two ways:

(a) Into *substantive dyes*, which color fabrics without a mordant, and *objective dyes*, which color fabrics with mordants only.

(b) Into *basic dyes*, usually a hydrochlorid of an aromatic amid, and *acid dyes*, the sodium salts of a sulfonic aromatic acid.

MORDANTS (from Latin *mordere*, to bite in), are substances like albumin, which combine with dyes, making double compounds; and with the basic dyes, acids, like tannic, or salts, like stannic chlorid and tartar emetic, precipitate in the fiber of the fabric *insoluble lakes*. Mordants, therefore, are substances which *fix colors on fabrics*.

THE FIBERS USED can be divided into *animal* or *vegetable*.

The *animal fibers* embrace *wool*, the hair of sheep;

hair of goats and camel, etc.; *silk*, the fibers from which the cocoons of the silk-worm are spun; *feathers* of the various fowl, etc.

The *vegetable* fibers embrace *cotton*, chiefly pure cellulose; *jute*, the hemp fiber; *linen*, the flax fiber; *straw*, *esparto*, etc.

PREPARATION OF THE FIBERS.—The fibers are generally washed to remove coloring material, grease, wax and dirt. This is frequently done by boiling with lime or soda-ash. These alkalis should, however, be used in moderation, excess weakens the fiber.

The fibers, washed free from the alkali, are next *bleached*. This is effected by the use of solutions of *bleaching powder*, $\text{Ca}(\text{Cl}_2\text{O})$ or sodium hypochlorite, NaClO . Potassium permanganate solutions followed by thiosulfates are also used. Wool contains about 50% of its weight of a fatty *suint*, or residue from evaporated perspiration, which must be freed by boiling it with alkalis.

Wool and silk can be bleached with sulfur dioxid.

Bleaching is necessary in almost every case to prevent the impairment of the color produced in the subsequent dyeing.

Dyeing consists in macerating the skeins of threads or pieces of the finished fabric in an acid or alkalin bath containing the dye. Almost all the colors have affinity for wool and silk, and no mordants are necessary. Not so with cotton; so few dyes affect cotton that invariably mordants must be employed.

A dye must of necessity be a colored substance, but

not all colored substances are necessarily dyes, unless they can fix themselves to the fabric in such a way that washing or rubbing cannot remove them. Thus, azobenzene is highly colored, but it will not dye fabrics. Likewise when silk or wool are placed in a solution of picric acid, they will be dyed a beautiful yellow; *calico* or other *cotton* material will also be colored yellow; but upon washing, the dye, while permanent in silk and wool, will wash out from the cotton fabric. Therefore, some substances may be dyes for a given material, but not for other materials. This property is common to many dyes.

Again, materials may be steeped in basic dyes, like *rosanilin*, which is *colorless* by itself; but if the material has previously been steeped in a mordant, precipitation of a *colloidal dye* with the mordant will be affected *in the fiber*, producing lasting *fast* (not washed out or bleached) colors.

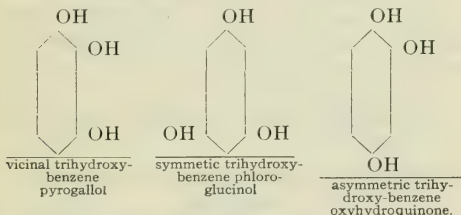
Indigo, on the other hand, is converted into *leuco-indigotin* by reducing agents, which render it soluble in water. The yarn or material saturated with this solution and wrung out, upon exposure, while drying will become dyed; the solution is converted to the insoluble *blue-indigotin* deposited in fibers of the fabric.

Various decoctions of tanning materials, such as nutgalls, oak-bark or sumach, upon the addition of some salt of iron, produce desirable "ink-blacks" which are "fast."

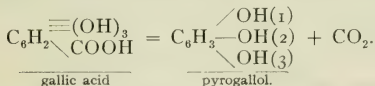
TRIATOMIC PHENOLS.

There are three triatomic (triacid) phenols; all isomeric $C_6H_3(OH)_3$ compounds:

Of these three isomers *pyrogallol* is the *most important*, *oxyhydroquinon* the least.



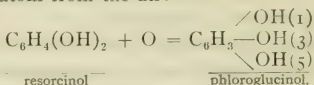
PYROGALLOL, $C_6H_3(OH)_3$ (Scheele, 1786), also called *pyrogalllic acid*, like all phenols, has acid properties. It is obtained by heating gallic acid:



Pyrogallol occurs in colorless needles, and melts at 132°C . It sublimes readily and is more soluble in water than in alcohol and ether. Pyrogallol readily absorbs oxygen, and for that purpose is employed in gas analysis. It is a prompt reducing agent, employed in photography and as external antiseptic in medicine. Pyrogallol is very poisonous.

PHLOROGLUCINOL, $C_6H_3(OH)_3$, *phloroglucin*, is found in certain resins as “dragon’s blood” and gamboge. It can be prepared by fusing resorcinol

with potash, whereby resorcinol takes up another oxygen atom from the air:



When dissolved in strong hydrochloric acid, it acquires a *pink color* in the presence of *pentoses*, for which it is a reagent. It melts at 218°C. , sublimes readily and is very soluble.

OXYHYDROQUINON is obtained by fusing quinol with caustic soda.

AROMATIC ALCOHOLS, ALDEHYDS AND KETONES.

The aromatic alcohols possess many properties in common with the paraffinic alcohols. They may likewise be produced by reactions analogous to those discussed under the Preparation of the Aliphatic Alcohols:

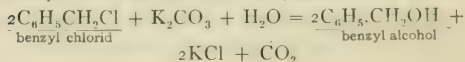
(1) By acting with moist silver oxid on a halid of a benzene homologue.

(2) By reducing an aromatic aldehyd or a ketone.

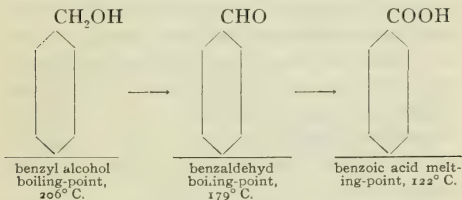
(3) By acting on amino derivatives of the aromatic hydrocarbons having the amino group in the alkyl (side chain).

The two following are typical aromatic alcohols:

BENZYL ALCOHOL, $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$, may be prepared by any of the above reactions or by boiling benzyl chlorid with a solution of potassium carbonate:



Properties.—This is the simplest aromatic alcohol; it occurs naturally in the balsams of tolu and Peru; boiling-point, 206° . It forms *derivatives and substitution products* like the aliphatic primary alcohols; thus, an aldehyd—the benzyl aldehyd—and an acid—the benzoic acid:

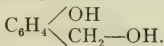


CINNAMYL ALCOHOL, *styrone*, $\text{C}_6\text{H}_5\text{CH}:\text{CH}.\text{CH}_2\text{OH}(\text{C}_9\text{H}_9\text{OH})$.

It occurs naturally in styrax; it is a crystalline body, melting-point, 32°C. , having a delightful hyacinth-like odor. It is obtained by reducing cinnamic aldehyd with sodium amalgam.

There is another class of aromatic alcohols and aldehyds distinguished, namely, those in which the hydroxyl group is present, both in the side chain and the nucleus; or the OH in the nucleus and CH_2OH group in the side chain. These are sometimes called—

PHENOL ALCOHOLS.—Example, *ortho-hydroxybenzyl alcohol*, or **SALICYL ALCOHOL**, *saligenin*,



Salicyl alcohol occurs as a *glucosid* in certain

willow barks under the name *salicin*. Salicin acted upon by the enzym emulsin yields saligenin. It may be also prepared by reducing salicylic aldehyd. It is a water-soluble, crystalline substance, melting at 82°C .

ANISYL ALCOHOL, *para-methoxy-benzyl-alcohol*, $\text{C}_6\text{H}_4(\text{OCH}_3)\text{CH}_2\text{OH}$, can be obtained from anisic aldehyd by treatment with alcoholic potash. Colorless crystals melting at 25° and boiling at 259° ; upon oxidation, converted into anisic aldehyd, and this into anisic acid.

VANIL-ALCOHOL, *vanillin alcohol*, $\text{C}_6\text{H}_3.\text{OH}.\text{OCH}_3.\text{CH}_2\text{OH}$, is formed from vanillin. Crystals melting at 115°C .

PIPERONYL ALCOHOL, *heliotropol*, is formed from piperonal similarly to vanil-alcohol by reducing solutions of the respective aldehyds with sodium-amalgam. Crystals melting at 57°C .

AROMATIC ALDEHYDS.—These, like the alcohols, are divided into those containing the CHO (aldehydic) group, either in the *side chain* or in the *nucleus*. They are analogous to the aliphatic aldehyds. Upon oxidation, they yield aromatic acids just like their aliphatic analogues. The *general methods of preparation* of the aromatic aldehyds is by:

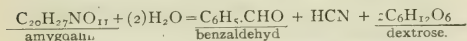
(1) Oxidation of the corresponding alcohol with nitric acid or potassium dichromate.

(2) By distilling a mixture of the corresponding acid calcium salt with calcium formate.

BENZALDEHYD, $\text{C}_6\text{H}_5\text{—CHO}$ (benzaldehydum), is artificially produced “oil of bitter almonds.”

It may also be obtained from natural oil of bitter almonds, peach- or cherry-kernel oil, etc. The U. S. P. requires at least 85% of benzaldehyd, and a boiling-point of 180° , specific gravity, 1.045, and be *free from hydrocyanic acid and chlorinated products*.

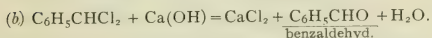
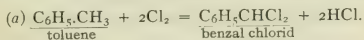
(1) *Benzaldehyd* may be obtained by macerating ground bitter almonds when, through the decomposition of *amygdalin* in the presence of water, benzaldehyd and hydrocyanic acid are formed:



(2) By the interaction and distillation of calcium benzoate and formate:

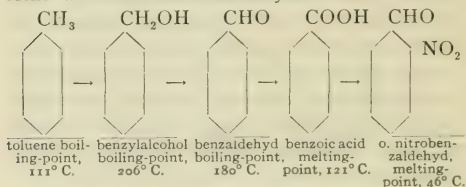


(3) Commercially, it is made by treating toluene with chlorin, which forms *benzal chlorid*, $\text{C}_6\text{H}_5\text{-CHCl}_2$; this heated under pressure with slaked lime gives benzaldehyd:



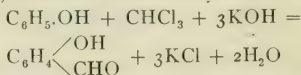
Description.—A colorless oil with a strong odor of bitter almonds, but free from hydrocyanic acid, upon oxidation yielding benzoic acid, which is sometimes seen as a deposit in the bottles containing old bitter almond oil. It is not poisonous when pure, but *its freedom from hydrocyanic acid should be*

established. With nitric acid it is converted into ortho- and meta-nitrobenzaldehyds.



To the class of *phenol aldehyds* or *oxyaldehyds* the following belong:

SALICYLIC ALDEHYD, *salicylal*, *orchideé*, oil of spirea (meadow-sweet), $\text{C}_6\text{H}_4.\text{OH}.\text{CHO}$, can be obtained by oxidizing salicin with potassium dichromate in presence of sulfuric acid; synthetically, it is made by heating phenol, chloroform and caustic potash. Salicylic aldehyd has an adhesive strong odor, reminding one of sweet clover, in the manufacture of the extract of which it enters; it has the specific gravity of 1.17, and boils at 196°C. Reaction, known as "Reimer's synthesis":



CINNAMIC ALDEHYD, "synthetic oil of cinnamon" or "cassia" (cinnaldehydum), $\text{C}_6\text{H}_5.\text{CH} = \text{CH}.\text{CHO}$. It can be obtained from the oils of cinnamon or cassia in which it occurs naturally, or it can be prepared synthetically by condensing benzaldehyd with acetaldehyd, evaporating the uncombined acetaldehyd and distilling with steam

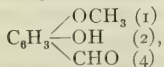
It can also—as can most aromatic aldehyds—be obtained by forming a bisulfitic compound with the oil of cassia. It occurs as a pale, yellowish liquid, having a strong cinnamon-like odor and taste, boiling at 250° C. and having a specific gravity of 1.047. It should be at least 95% pure and free from *chlorinated* bodies.

ANISIC ALDEHYD, $C_6H_4 \begin{matrix} \diagup OCH_3(1) \\ \diagdown CHO(4) \end{matrix}$, anisal,

“hawthorn oil,” aubépine, can be synthetically obtained by oxidizing fennel or anise oil with nitric acid. Chemically, it is *para*-methoxy benzaldehyd, a fragrant oil, boiling at 246° C., and having a specific gravity of 1.126 (15°); at a low temperature, solidifying. Upon exposure it is oxidized to anisic acid. With cumarin and orris tincture, in alcoholic solutions, it constitutes the “new-mown hay” extract.

PROTOCHATECHUIC ALDEHYD, $C_6H_3(OH)_2-CHO$. It may be prepared from pyrocatechin with chloroform and caustic potash (Reimer’s reaction). It melts at 150° and is chiefly of interest because of its close relation to *vanillin* and *heliotropin*.

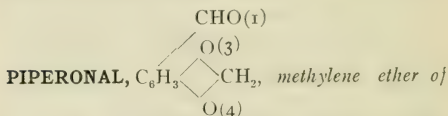
VANILLIN, *methylprotocatechuic aldehyd*,



occurs naturally in vanilla to which it imparts its delicious odor and flavor. It can be prepared synthetically by “Reimer’s synthesis” from monomethyl ether of catechol ($C_6H_4 \begin{matrix} \diagup OH \\ \diagdown OCH_3 \end{matrix}$ guaiacol).

Of late it has been prepared by oxidizing eugenol (constituent of clove oil) with ozone. Vanillin is a delightfully fragrant substance, with an odor of vanilla, melting at 80° C. and boiling at 285° C. When 2.5 % of vanillin is mixed with 97.5% of sugar, "vanillin sugar" is produced which can be used, weight for weight, in place of the best vanilla bean.

CUMINIC ALDEHYD, $C_9H_{11}CHO$, is a constituent in the volatile oils of the *umbelliferæ* (cummin, caraway and water hemlock).



protocatechuic aldehyd, heliotropin, may be obtained by oxidizing piperic acid. Small fragrant crystals, with a flowery odor of bitter almonds, melting at 37° C. Recently it has been prepared by oxidizing isosafrol with pyrochromic mixture diluted with water. Heliotropin possesses a delightful clinging odor of the white heliotrope flower, and mixed with alcohol its 2% solution with cumarin and oil of jasmin forms a fragrant "heliotrope extract."

AROMATIC KETONES are analogous with the fatty ketones; their general formula is $R - CO - R'$ —one of the two R representing an aromatic radicle.

ACETOPHENONE is a typical aromatic ketone. Chemically, it is *phenylmethylketone* or *acetyl benzene*, $C_6H_5 - CO - CH_3$. It is produced by

distilling a mixture of calcium benzoate and calcium acetate:



Acetophenone crystallizes in large transparent plates, melting at 21°C ., and boiling at 200°C ., and possessing an odor like benzaldehyd. It is known in pharmacy as *hypnone*, and in medicine employed as a soporific.

BENZOPHENONE, $\text{C}_6\text{H}_5.\text{CO}.\text{C}_6\text{H}_5$, *diphenyl ketone*, is produced by the dry distillation of calcium benzoate:



It occurs in colorless prisms, melting at 49°C .; on reduction with sodium amalgam, it produces a corresponding secondary alcohol, $\text{C}_6\text{H}_5.\text{CHOH}.\text{C}_6\text{H}_5 = \text{diphenyl alcohol}$.

THE QUINONES may be described as *aromatic diketones*. *Benzoquinon*, the representative of the class commonly known as *quinon*, is usually obtained by the *oxidation* of *para-derivatives*, such as *para- amidophenol* or *hydroquinol*:

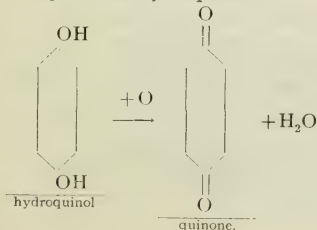


TABLE OF AROMATIC ACIDS AND HYDROXY ACIDS.

Monobasic Saturated Acids.

	Melting-point
Benzoic acid, $C_6H_5.COOH$	121°
Phenylacetic acid, $C_6H_5.CH_2.COOH$	76°
Toluic acids, $C_6H_4(CH_3).COOH$	$\left\{ \begin{array}{l} o-, 102^\circ \\ m-, 110^\circ \\ p-, 180^\circ \end{array} \right.$
Hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$	49°
Mesitylenic acid } $C_6H_3(CH_3)_2COOH$	166°
Xylylic acids } $C_6H_3(CH_3)_2COOH$	126°
	163°
Cumic acid, $C_6H_4(C_3H_7)COOH$	116°

Polybasic Saturated Acids.

Phthalic acids, $C_6H_4 \begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array}$ }	$\left\{ \begin{array}{l} o-, 213^\circ \\ m-, 300^\circ + \\ p-, \dots \end{array} \right.$
Trimesic acid, $C_6H_3(COOH)_3$	300°
Pyromellitic acid, $C_6H_2(COOH)_4$	264°
Benzene-penta-carboxylic acid, $C_6H(COOH)_5$
Mellitic acid, $C_6(COOH)_6$

Unsaturated Acids.

Cinnamic acid, $C_6H_5CH=CH.COOH$	133°
Atropic acid, $C_6H_5.C \begin{array}{l} \diagup CH_2 \\ \diagdown COOH \end{array}$ }	106°
Phenyl-propionic acid, $C_6H_5.C=C.COOH$	136°

Phenol Acids and Alcohol Acids.

Salicylic acid, $C_6H_4(OH)COOH$	155°
m- and p- oxybenzoic acids, $C_6H_4(OH)-COOH$	$\left\{ \begin{array}{l} m-, 200^\circ \\ p-, 210^\circ \end{array} \right.$

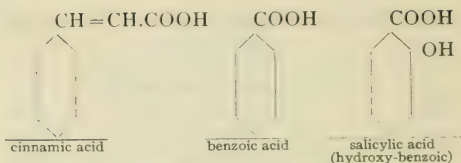
Anisic acid, $C_6H_4(OCH_3)COOH$	184°
Oxytolulic acids, $C_6H_3(CH_3)\left\langle \begin{smallmatrix} OH \\ COOH \end{smallmatrix} \right\rangle$
Melilotic acid, $C_6H_4(OH)CH_2CH_2COOH$	128°
Mandelic acid, $C_6H_5.CHOH.COOH$	118°
Tropic acid, $C_6H_5.CH\left\langle \begin{smallmatrix} CH_2OH \\ COOH \end{smallmatrix} \right\rangle$	117°
Protocatechuic acid, $C_6H_3(OH)_2COOH$	199°
Vanillic acid, $C_6H_3(OH)(OCH_3).COOH$	207°
Orsellinic acid, $C_6H_2(CH_3)(OH)_2COOH$	176°
Gallic acid, $C_6H_2(OH)_3.COOH$	222°
Tannic acid, $C_{14}H_{10}O_9$
Quinic acid, $C_6H.H_6(OH)_4COOH$	162°

Unsaturated Phenol Acid.

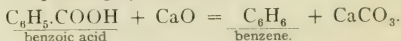
Coumaric acid, $C_6H_4(OH)CH = CH-$ COOH	$\left\{ \begin{array}{l} \text{o-, } 208^\circ \\ \text{p-, } 206^\circ \end{array} \right.$
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AROMATIC ACIDS.

These acids are also known as *carboxylic*, and can be produced by methods analogous to those employed in the production of the aliphatic acids. These acids are divisible into three classes: Those containing the carboxyl group in the side chain, as cinnamic acid, $C_6H_5.CH = CH.COOH$; those containing the carboxyl group on the nucleus, as benzoic acid, $C_6H_5.OH$, and those which besides the carboxyl group contain also a hydroxyl group. This third class of acids is known as "*phenol- or alcohol-acids*"; example, salicylic acid, $C_6H_5.OH.COOH$.



General Properties.—All the aromatic acids are crystalline; all sparingly soluble in water, but freely in the organic solvents. They can be distilled without decomposition, but when distilled with lime they are decomposed, losing carbon dioxide and forming a corresponding hydrocarbon:



BENZOIC ACID, $\text{C}_6\text{H}_5\text{COOH}$, was so named because it was first obtained from the balsamic resin—benzoin.

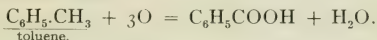
Like all the organic acids, it can be *produced by* one of the following *general methods*:

- (1) By the oxidation of the corresponding aromatic alcohols and aldehydes.
- (2) By hydrolysis of a corresponding nitril.
- (3) By the oxidation of the side chain of a cyclic hydrocarbon containing such.

The general reactions may be exemplified by equations showing the production of benzoic acid:

- (1) $\frac{\text{C}_6\text{H}_5.\text{CH}_2\text{OH}}{\text{benzyl alcohol}} + 2\text{O}_2 = \frac{\text{C}_6\text{H}_5.\text{COOH}}{\text{benzoic acid}} + \text{H}_2\text{O}.$
- (2) $\frac{\text{C}_6\text{H}_5.\text{CHO}}{\text{benzaldehyde}} + \text{O} = \text{C}_6\text{H}_5.\text{COOH}.$
- (2) $\frac{\text{C}_6\text{H}_5.\text{CN}}{\text{benzo nitril}} + 2\text{H}_2\text{O} = \text{C}_6\text{H}_5.\text{COOH} + \text{NH}_3.$

The most common method of producing benzoic acid is the third one—oxidizing a side chain of a hydrocarbon; thus, by the oxidation of toluene by dilute nitric acid:



Properties of Benzoic Acid.—Glistening colorless needles, melting at 121°C . and boiling at 250° ; sparingly soluble in water, freely in the organic solvents.

Benzoic acid is also produced from “hippuric acid” as well as toluene; but in pharmacy for internal use, *only that sublimed from benzoïn should be employed*:

Benzoic acid is used as a preservative in foods, but its use *should be prohibited*, in that it is converted into phenol by the liver and acts as a cumulative systemic poison.

Tests.—(1) Aqueous solutions of benzoic acid and its soluble salts give with ferric chlorid *salmon-colored* precipitates.

(2) A benzoate dissolved in alcohol to which a few drops of H_2SO_4 have been added, upon heating, yields the characteristic odor of ethyl benzoate.

(3) Silver nitrate added to a solution of a benzoate is precipitated as a crystalline silver benzoate which, on ignition, yields a residue of 47.1% of silver.

DERIVATIVES OF BENZOIC ACID.

THE ESTERS.—These can be prepared by methods analogous to the paraffinic esters.

METHYL BENZOATE, $\text{C}_6\text{H}_5\cdot\text{COOCH}_3$, is a

colorless oil, boiling at 199° C. and having a fragrant odor. Synonym, "niobe oil."

ETHYL BENZOATE, $C_6H_5 \cdot COOC_2H_5$, a fragrant liquid, boiling at 212° C.

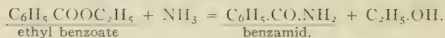
BENZYL BENZOATE, $C_6H_5 \cdot COO \cdot C_6H_5$, is found naturally in cinnamein (oil of balsam peru); may be obtained from benzyl chlorid and benzyl alcohol.

BENZOYL CHLORID, $C_6H_5 \cdot CO \cdot Cl$, is obtained by treating benzoic acid with phosphorus pentachlorid. It bears the same relation to benzoic acid that acetyl chlorid does to acetic acid and, like the latter, it is an important reagent in organic synthesis.

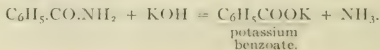
It is a colorless oil with a very irritating odor, and boils at 198° C. With water it is gradually decomposed into benzoic and hydrochloric acids.

BENZOIC ANHYDRID is produced when benzoyl chlorid is treated with sodium benzoate. It is a crystalline substance, melting at 42° C., and has the formula $(C_6H_5 \cdot CO)_2O$. The monovalent *benzoyl group* has the formula $C_6H_5 \cdot CO$.

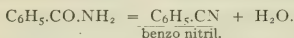
BENZAMID, $C_6H_5 \cdot CO \cdot NH_2$, is a typical example of an aromatic amid. It can be produced in much the same way as acetamid of the fatty compounds:



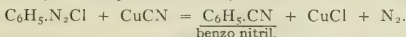
Benzamid occurs in sparingly soluble crystals, melting at 130° C. When heated with alkalis it is decomposed, yielding ammonia and a corresponding salt:



BENZONITRIL or *phenyl cyanid*, $C_6H_5.CN$, can be prepared by treating benzamid with dehydrating agents:



It may also be prepared from an anilin derivative—diazobenzene chlorid—by treating it with cuprous cyanid (*Sandmeyer's reaction*):



Benzonitril has the odor and appearance of nitrobenzene, but it boils at $191^\circ C$.

HALOGEN DERIVATIVES OF BENZOIC ACID.—

Benzoic acid is attacked by the halogens, although not so readily as the hydrocarbons. The following are the more important products:

META-BROMBENZOIC ACID, $C_6H_4.Br.COOH$, melting at $155^\circ C$.

ORTHO-BROMBENZOIC ACID, $C_6H_4.Br.COOH$, melting at $147^\circ C$.

PARA-BROMBENZOIC ACID, $C_6H_4.Br.COOH$, melting at $251^\circ C$.

All the above acids last mentioned are made by oxidizing corresponding bromtoluenes with nitric acid.

When nitric acid, in presence of sulfuric acid, acts on benzoic acid, the following nitro derivatives are obtained:

ORTHO-NITROBENZOIC ACID, $C_6H_4.NO_2.COOH$; melts at $147^\circ C$.

META-NITROBENZOIC ACID, $C_6H_4.NO_2.COOH$; melts at $141^\circ C$.

PARA-NITROBENZOIC ACID, $C_6H_4.NO_2COOH$; melts at $238^\circ C$.

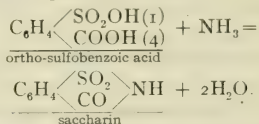
ANTHRANILIC ACID is ortho-amidobenzoic acid,
 $C_6H_4 \begin{array}{l} \swarrow COOH(1) \\ \searrow NH_2(2) \end{array}$.

It is produced by boiling indigo with caustic alkali.

When heated with sulfuric acid, benzoic acid is converted into mono-sulfobenzoic acid,

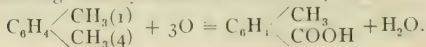


Ortho-sulfobenzoic acid is obtained by oxidizing toluene ortho-sulfonic acid. This acid treated with ammonia yields *sulfo-benzo-imid*, commonly known as "*saccharin*," *glucin*, *garantose*, etc.:



SACCHARIN (benzosulphinidum), *benzosulfinid*, is about 450 times as sweet as sugar, and one gram of it will afford the sweetening equivalent to 1 pound of granulated sugar. It is used for this purpose and in this proportion to *sweeten* the *food of diabetic patients*. Its use as a sweetener of ordinary foods should be prohibited, as its use is productive of bad effects on the plasma of the blood.

There are *three* isomeric *toluic acids* (o. m. p.), which may be produced by oxidizing the corresponding three xylenes with nitric acid; thus:



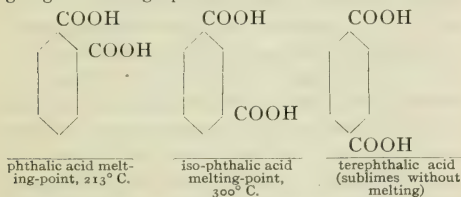
ORTHO-TOLUIC ACID, $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown COOH \end{smallmatrix}$, melts at $103^{\circ} C$.

META-TOLUIC ACID, $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown COOH \end{smallmatrix}$, melts at $110^{\circ} C$.

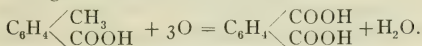
PARA-TOLUIC ACID, $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown COOH \end{smallmatrix}$, melts at $180^{\circ} C$.

All the toluic acids are crystalline and all resemble benzoic acids, and each, like benzoic acid, furnishes a corresponding chlorid, amid, anilid, nitro acid, etc., by the usual methods.

The *three phthalic acids* analogous to the foregoing have the graphic formulas:



The **PHTHALIC ACIDS** above can be obtained by treating corresponding toluic acids with potassium permanganate in alkalin solution:



When strongly heated, phthalic acid yields:

PHTHALIC ANHYDRID, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$, melting at 128° and boiling at 284° . *Phthalimid* is obtained

from the anhydrid by heating it with ammonia. It melts at 229°C .

CUMIC ACID, para-isopropylbenzoic acid, $\text{C}_3\text{H}_7\text{-C}_6\text{H}_4\text{.COOH}$, is obtained by the oxidation of cuminol.

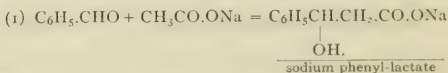
UNSATURATED AROMATIC ACIDS. The following are representatives:

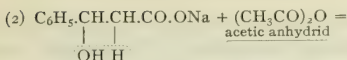
Phenylacetic acid, $\text{C}_6\text{H}_5\text{.CH}_2\text{COOH}$, melting at 76.5° .

Phenyl propionic acid, $\text{C}_6\text{H}_5\text{.CH}_2\text{.CH}_2\text{.COOH}$, melting at 47° .

Cinnamic acid, $\text{C}_6\text{H}_5\text{.CH:CHCOOH}$, also called *phenylacrylic acid* belongs to the class of *unsaturated aromatic acids*. It occurs naturally in the balsamic resins—tolu, peru and styrax—and may be synthetically prepared by "*Perkins' reaction*." This last is also a general method for the preparation of the unsaturated aromatic acids, and depends upon the heating of an aldehyd (either aliphatic or aromatic, depending upon the product desired) with the sodium salt of a fatty acid and its or some other anhydrid. The heating at 180° is continued for several hours. Condensation occurs, splitting off water, which is absorbed by the anhydrid. The anhydrid is thus converted into an acid which liberates the corresponding acid from its sodium salt.

Cinnamic acid is produced by the above reaction from a mixture of benzaldehyd, acetic anhydrid and anhydrous sodium acetate, which is heated to 180° .





Cinnamic acid is readily soluble in hot water; it melts at 133°C . and sublimes at 300°C .

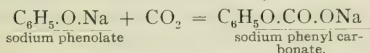
THE HYDROXY ACIDS include the important—

SALICYLIC ACID, *ortho-hydroxy benzoic acid*,

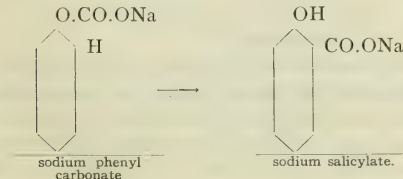
$\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{OH} \\ \diagdown \text{COOH} \end{matrix} \quad (2)$, which occurs naturally in oil of wintergreen (*gaultheria*) as a methyl ester (methyl salicylate). It can be obtained (1) by fusing salicin with caustic soda; (2) by boiling oil of wintergreen with potassium hydroxid solution, whereby potassium salicylate is formed. Methyl alcohol being liberated.



(3) by heating phenol with caustic soda in a current of carbon dioxid—"Kolbe's synthesis".



When this is heated to 200°C ., sodium salicylate forms:

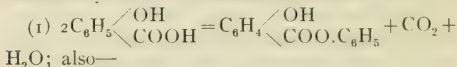


Thus, the high heat effects the intramolecular change. Sodium salicylate is decomposed with sulfuric acid, and salicylic acid is set free.

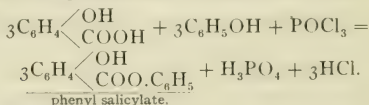
Properties.—Salicylic acid occurs in fine, white, sparingly soluble crystals melting at 155° C. and readily soluble in the organic solvents. It is a valuable external antiseptic and a preservative, but *unsuited for internal administration*. For this later purpose only its sodium salt, which has been prepared from the oil of wintergreen, should be employed. The same may be said of all its other salts.

Tests.—With ferric chlorid soluble salicylates give a violet-red color (distinguished 1 in 500,000 parts).

SALOL is the *phenylester of salicylic acid*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{COC}_6\text{H}_5 \end{smallmatrix}$, *phenyl salicylate*; it is obtained when salicylic acid is heated alone to 210° C.:



(2) By heating phenol with salicylic acid in the presence of phosphorus oxychlorid:



Properties.—A white, crystalline, tasteless powder, converted in the body to phenol and salicylic acid by the pancreatic juice (it is insoluble in the peptic juices), and excreted by the urine as such. It possesses an aromatic odor, is insoluble in water

and melts at 43° C. Owing to its low melting-point and insolubility in the stomach, it is used for the coating of *enteric pills*.

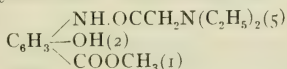
SANOFORM, C_6H_2 $\begin{array}{l} \nearrow COOCH_3 \\ \text{---} OH \\ \searrow I_2 \end{array}$, is *di-iodo-salicylic*

methylester, prepared by acting on the oil of winter-green with iodine. Insoluble in water, soluble in alcohol; it melts at 100° C.

SALOPHEN, *acetyl para-amidophenyl salicylate*, $C_6H_4(OH)COO.C_6H_4NH.COCH_3$, a substitute for salol, it splits in the intestines into acetyl para-amido-phenol and salicylic acid. It melts at 187° C.

SALIPYRIN is obtained by heating together 57.7 parts of antipyrin with 42.3 parts of salicylic acid, cooling and crystallizing from hot alcohol. Sparingly soluble, it melts at 92° C.

NIRVANIN, a hydrochlorid of diethyl-glycocoll-amido-oxybenzoic methyl ester. It is used for producing local anesthesia as a substitute for cocaine which is more toxic, also used in dental practice in 2 to 5% solutions. It has the formula



ORTHOFORM is related to *nirvanin* in properties, but is more toxic. It is the *methylester of amido-*

hydroxy benzoic acid = C_6H_3 $\begin{array}{l} \nearrow NH_2(1) \\ \text{---} OH(2) \\ \searrow COOCH_3(4) \end{array}$.

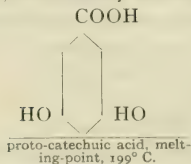
ASPIRIN is *acetyl salicylic acid*, $C_6H_4 \begin{smallmatrix} \diagup OOCCH_3 \\ \diagdown COOH \end{smallmatrix}$.

BETOL is the *naphthol ester of salicylic acid*,
 $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown COO.C_{10}H_7 \end{smallmatrix}$.

METHYL SALICYLATE, $C_6H_4 \begin{smallmatrix} \diagup OH \\ \diagdown COO.CH_3 \end{smallmatrix}$, is the proximate principle found in the oil of gaultheria (wintergreen) and oil of betula. It can be obtained synthetically by distilling a mixture of salicylic acid, methyl alcohol and sulfuric acid. For flavoring purposes methyl salicylate (methylis salicylas), oil of gaultheria and the oil of betula may be said to be identical; for internal administration, however, *only the last two should be used*.

Among the *dihydroxy (dioxy) benzoic acids*, the following may be mentioned.

PROTOCATECHUIC ACID, $C_6H_3(OH)_2.COOH + H_2O$, is one of six isomeric dihydroxy benzoic acids. It is found in many of the commoner resins, coloring matters, also in many tannins. It has the structure:



COUMARIN is the *inner ester (lactone)* of *ortho-hydroxy, cinnamic acid*, $C_6H_4 \begin{smallmatrix} \diagup CH:CH \\ \diagdown O-C=O \end{smallmatrix}$; it oc-

curs in very white crystals, possessing a very fragrant odor of woodruff, tonka bean and new-mown hay, of which it is a constituent. It is prepared from salicylaldehyd by the *Perkins reaction*, and is much used in perfumery and soaps; it blends well with aubepine and heliotropin, and melts at 67° .

TRIHIDROXYBENZOIC ACIDS.—Among these but two, gallic and ellagic acids, are of importance.

GALLIC ACID, $C_6H_2(OH)_3COOH$. It is prepared by exposing moistened nutgalls to the air, when, by influence of a certain peculiar fermentation, tannin is converted into gallic acid. It can be prepared from gallotannic acid, of which it is an anhydrid, by boiling it with dilute acids. It can be separated from gallotannic acid because it is soluble in aqueous ether.

Gallic acid occurs in colorless crystals, melting at $220^{\circ} C.$, readily soluble in hot water, less so in cold water.

Tests.—(1) With ferric chlorid a *deep blue ink* is produced.

(2) With potassium cyanid a pink precipitate is produced, which fades on standing, but reappears on shaking.

(3) It does not precipitate gelatin (distinction from the tannins).

ELLAGIC ACID is a yellow, crystalline, insoluble substance, closely related to gallic acid and found together with certain tannins, as in sumac, etc.

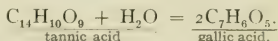
DERMATOL is the basic bismuth gallate, $Bi(OH)_2 \cdot C_6H_2(OH)_3CO_2$; a yellow, insoluble powder.

AIROL is the oxyiodid of basic bismuth gallate, $C_6H_2(OH)_3Bi \begin{smallmatrix} \text{OH} \\ \diagup \text{I} \end{smallmatrix}$; a greenish, voluminous, insoluble powder.

THE TANNINS.

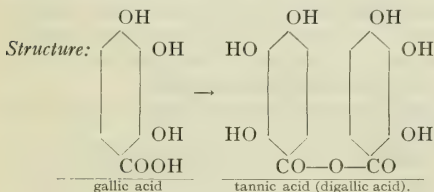
This name, as well as that of "tannic acids," is applied to a large number of substances which have the property of forming insoluble compounds with the albumin of the raw hides by which they are absorbed.

The ordinary "tannic acid" is the monobasic *gallotannic acid*, obtained from nutgalls (which contain 50% of tannin); chemically, it is digallic acid; *i. e.*, a condensation product of two molecules of gallic acid with the elimination of one molecule of water. And in reality, upon heating tannic acid, gallic acid is produced:



TANNIC ACID (acidum tannicum), $HC_{14}H_{10}O_9$, gallotannic acid, or digallic acid. Prepared from nutgall by maceration with water and extraction with ether. When heated in presence of moisture by chemical reaction it is converted into gallic acid. Light yellowish, amorphous powder; strongly astringent taste; soluble in 0.34 part water and in 0.23 part alcohol, in 1 part glycerin with heat, freely in dilute alcohol; insoluble in other solvents; with ferric chlorid it produces bluish-black color which upon addition of lime-water is converted into bluish-

white and, with excess of lime-water, pinkish. It precipitates gelatin, alkaloids and metallic salts, and with potassium chlorate and other strongly oxidizing agents, it is explosive. When in solution, it forms ink with iron salts, and its preparations should not be brought in contact with iron vessels or spatulas. (Preparations: Collodium stypticum, glyceritum, troche, unguentum.)



In the arts it is used as a mordant for certain dye-stuffs, and in the manufacture of inks; but for the tanning of leather cheaper varieties of tannin are employed.

OTHER TANNINS.

Tannin is a substance peculiar to the vegetable kingdom and widely distributed. Various modifications of it are known. Thus in nutgall, as *gallotannic acid*, in oak as *quercitannic acid*, and in catechu, krameria and cinchona as *catechu*, *kramertannic* and *cinchotannic acid*, respectively. They are composed of C, H and O in varying proportions. Tannins are usually amorphous; soluble in water, alcohol and glycerin. Their solutions are

acid in reaction and precipitated by most of the metallic salts and the alkaloids. When boiled with dilute acids they split into glucose and phlobaphene, *being therefore regarded as glucosids*, their chief property being that they form insoluble compounds with gelatin and, therefore, are used in tanning of leather. They are astringent when applied to mucous membranes, and upon this depends their therapeutic value. With iron salts the tannins produce characteristic colorations from green to blue-black, the different shades allowing of their being identified and distinguished.

Other important sources of tannin are among the following:

SUMACH, leaves of, *Rhus coriaria* and *Rhus glabra*.

OAK, bark of, *Quercus alba*.

MYROBALANS, fruit of *Terminalia chebula*.

CUTCH, extract of the wood of *Acacia catechu*.

HEMLOCK, bark of *Abies canadensis*.

POMEGRANATE, bark of *Punica granatum*.

CHESTNUT, bark of *Castanea vesca*.

TANNING is the process of *treating hides with tannin, to prevent putrefactive changes and to render the so-produced leather permanently flexible*.

Tanning is effected by first soaking the raw hides in milk of lime to remove the hair and at the same time to swell the skin. The lime is next dissolved out by soaking the skins in "old tan liquor" (containing lactic and citric acids—produced by fermentation) or in fermenting dung. The skins are then digested

(steeped) in "tan liquor"—an *aqueous extract of tannin*, which precipitates the albumin of the skin, which is absorbed by the skin, *rendering it insoluble flexible and porous—or leather*.

During the past few years the tanning of leather has been effected by other substances; thus, *chrome alum* has made the "chrome-tanned" American leather famous for its good wearing and elastic qualities. *Other chromates and formaldehyd* have also been successfully used.

THE GLUCOSIDS.

The term "glucosid" or "glycosid" is applied to a class of proximate principles which may be regarded as *ethers* chemically.

The term glucosid was applied to these, owing to the fact that they are readily hydrolized into "glucose" when warmed with dilute acid or alkalin liquids, and in this respect they differ from the true ethers; also, by the enzymes: if one of these is of albuminous nature, glucose is formed.

The foregoing class of *tannins* are frequently classed with the glucosids.

For convenience we will discuss the neutral principles under this head.

The neutral principles include: aloin, chrysarobin, emodin, elaterin, santonin, picrotoxin, podophylo-toxin.

The glucosids include: arbutin, salicin, strophanthin, quercitrin, amygdalin, sinigrin and the glucosids of *digitalis*.

They all contain C, H and O. While some contain also N in addition, and others S. Thus, *amygdalin*, $C_{20}H_{27}NO_{11}$, is nitrogenized, while *sinalbin*, $C_{30}H_{42}N_2S_2O_{15}$, and *sinigrin*, $C_{10}H_{16}NS_2 \cdot KO_9 + H_2O$ are sulfurated glucosids. They are nearly all insoluble in water, though readily soluble in alcohol. *Their English names end in "in," the Latin in "inum."* To distinguish them from alkaloids ending in "*ine*," Latin "*ina*."

The neutral principles are solid, crystalline substances derived from plants. They are composed of C, H and O; insoluble in water, freely soluble in alcohol, sparingly in ether and chloroform. They differ from the glucosids in not being split into glucose, and from alkaloids in that they are not precipitated by tannin and other alkaloidal reagents. Sometimes they are classed as "bitter principles," on account of their taste.

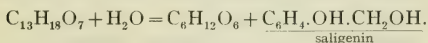
ALOIN (*aloinum*) $C_{17}H_{18}O_7$, obtained from several varieties of aloes, chiefly Curacao aloes. Prepared by extracting aloes with acidulated boiling water, concentrating and crystallizing from warm, dilute alcohol. A crystalline powder of yellowish color; soluble in 65 parts water, 10 parts alcohol. Used in pills as a cathartic. Dose, 0.06. Preparation: Pil. laxat. comp.

ELATERIN (*elaterinum*), $C_{20}H_{28}O_5$. Obtained from elaterium, which is deposited in the juice of the fruit of *ecbaliu elaterium*. Minute white crystals, sparingly soluble in the solvents, except in 22 parts chloroform. Used in the official 10%

trituration as hydrogogue cathartic. The Clutterbucks elaterin is the most reliable. Dose, 0.03.

PICROTOXIN (*picrotoxinum*) is soluble in 240 parts water and 9 parts alcohol. Used in 0.001 gm. doses.

SALICIN (*salicinum*), $C_{13}H_{18}O_7$, a glucosid obtained from several species of the salix and populus by digestion with lead oxid, extraction with water, purification with charcoal and crystallization. Silky needles, soluble in 21 parts water, 71 parts alcohol, insoluble in other solvents. Colored violet with ferric chlorid; sulphuric acid dissolves it with red color. Saliva resolves it into saligenin and glucose. Used in rheumatism.



SANTONIN (*santoninum*), $C_{15}H_{18}O_3$, the inner anhydrid or lactone of santonic acid. Obtained from santonica by boiling levant worm-seed with calcium hydroxid, decomposing this salt with HCl, dissolving in hot alcohol, purifying with charcoal and crystallizing. Flat, prismatic crystals; soluble in 35 parts alcohol, 78 parts ether, 2.5 parts chloroform. Turns yellow when exposed to light. Used in the official troche, containing 0.03 gm. in each, as a worm remedy.

CHRYSAROBIN (*chrysarobinum*), a neutral principle extracted from goa powder. A pale, orange-yellow powder, darkens on exposure, soluble in 150 parts boiling alcohol, insoluble in water. Used in ringworm and other skin diseases. Dose, 0.03 gm.

With oxidizing agents it is oxidized to chrysophanic acid. Preparation: Unguentum 6%.

STROPHANTHIN (*strophanthinum*), $C_{40}H_{66}O_{19}$, a glucosid or mixture of glucosids obtained from *strophanthus*. Yellowish-white, crystalline powder, intensely bitter, very soluble in water and dilute alcohol, insoluble in other solvents. Used to regulate heart action. Dose, 0.0003 gm. ($\frac{1}{2500}$ grain).

Glucosids obtained from Digitalis purpurea:

DIGITOXIN, $C_{28}H_{46}O_{10}$, most active glucosid of digitalis leaves. White, crystalline powder, almost insoluble in water, soluble in alcohol and chloroform. Dilute acids decompose it into *digitoxose*, $C_6H_{12}O_4$ (a-sugar), and *digitoxigenin*, $C_{22}H_{32}O_4$. Dose, 0.00025 gm. ($\frac{1}{250}$ grain).

DIGITALIN, "French," yellow amorphous powder, soluble in 2000 parts of water, very soluble in alcohol and chloroform; consists chiefly of a glucosid, physiologically identical with digitoxin. Dose, 0.00025 gm. ($\frac{1}{250}$ grain).

DIGITALIN, "German," yellowish-white powder, soluble in water and alcohol, almost insoluble in chloroform; consists of a mixture of glucosids *digitalin*, amorphous *digitonin* and *digitalein*. Dose, 0.001 gm. ($\frac{1}{64}$ grain).

DIGITALIN cryst. (Kiliani), identical with *digitonin* cyst. $C_{27}H_{46}O_{14} + 5H_2O$ almost insoluble in water, ether and chloroform. *Physiologically inactive*.

DIGITALEIN, white amorphous powder, soluble in water and alcohol. A heart poison.

QUERCITRIN, $C_{36}H_{38}O_{20}$, is present in *Quercus tinctoria*, tea, which, when hydrolyzed, yields a yellow dye, *quercetin*, and *ramnose*, a sugar.

EMODIN, $C_{15}H_{10}O_5$, is present in *Cascara sagrada*, *rhubarb* and *buckthorn bark*.

ARBUTIN ($C_{12}H_{16}O_7$), found in *bearberry leaves*, yields hydroquinone and dextrose on hydrolysis.

PICROTOXIN ($C_{30}H_{34}O_{13}$), found in *Cocculus indicus*, is highly poisonous.

PODOPHYLLOTOXIN, $C_{23}H_{24}O_9 + H_2O$), occurs in the resin of *Podophyllum peltatum*.

CHAPTER XXXVI.

THE GUMS.

THE gums are a class of amorphous substances frequently produced by the degeneration of the tissue of plant cells. The gums are divided into two classes: (a) The *soluble* or *true* gums, of which **ACACIA** or *gum arabic*, an exudation from *Acacia senegal*, is a type, and (b) *insoluble* gums, which absorb large quantities of water with which they form jellies, but do not dissolve in it. To this second class belongs **TRAGACANTH**, from *Astragalus gummifer* and other varieties of astragalus.

ACACIA, chemically, is the arabinate salt of calcium and magnesium, a complex compound, *precipitated* by alcoholic and ethereal tinctures, ferric chlorid, borax and lead salts. Its mucilage (*Mucilago acaciæ*) and powder are useful for suspending resinous, fatty or oily substances in aqueous media, forming *emulsions*.

TRAGACANTH, chemically, is composed of *bassorin* or *tragacanthin*, $C_{12}H_{20}O_{10}$, and calcium salt of *gummic acid*, which is not identical with arabic acid. Tragacanth occurs in flakes which can be pulverized when heated to $50^{\circ}C$. It is also employed in making emulsions and troches and for suspending insoluble powders in water.

RESINS are solid, usually amorphous, vegetable products with a conchoidal fracture. Soluble in alcohol, fixed oils, but not in water. Transparent or semitransparent, readily fusible and inflammable. Some contain acids, and with the alkalis are capable of forming soaps, others are not saponifiable. Composition: Resins are mixtures of different compounds of C, O and H. *Shellac*, for example, consists of 5 different resins and a coloring matter. *Amber* is a mixture of several resins with succinic acid. *Sandarac* consists of three insoluble resins and a bitter principle soluble in water. They are, perhaps, the oxidation products of volatile oils, judged from the fact that they are always associated with it in plants. Some resins, like *amber*, *elemi*, *copal*, *dammar*, *kauri gum*, *shellac* and *asphalt*, all unofficial, are used for the manufacture of varnishes; others, like *resina*, *guaiac*, *mastic*, are used in medicine. *They are divided into:* (1) *Resins obtained from oleoresins*, as the residue from distillation. (2) *Natural exudations*. (3) *Prepared resins* obtained by precipitating *extracts* of drugs with acidulated water, sometimes called "resinoids." (4) *Balsamic resins* or "balsams." Member of the first class **RESINA**, common rosin or colophony, is the residue after distilling the volatile oil (oil of turpentine) from the oleoresin of turpentine (pitch). Melting point, 100° C. Dark, amber-colored mass, soluble in alcohol, ether and the oils. Contains abietic anhydrid. Used mainly for varnishes, ointments,

soaps and plasters. (Off. Prep.: Ceratum Resinae Comp.) **NATURAL GUMS** include all the varnish "gums" mentioned above and that of **GUAIACUM** (Guaiaci resina). It is found in the heart wood. A very complex substance consisting of *guaiacic acid*, guaiac yellow, *guaretic acid*, betaresin, also small proportion of gum. It is soluble in alcohol and caustic potash, but insoluble in turpentine and benzol. The powder is whitish, but turns green on exposure to light and air, the depth of the color being indicative of the age of the powder. Used as a stimulant, diuretic and alterative. Sometimes given as an emulsion in rheumatism and in pastils for sore throat. (Off. Prep.: Tincture and Ammoniated Tr.). **MASTIC** (mastiche). Obtained from vertical incisions into the bast layer of the trunk of the tree and the larger branches. Contains *mastichic acid* about 90%, soluble in alcohol; *masticin*, soluble in hot alcohol, a trace of volatile oil. Mild astringent, also used for cements and varnishes. (Off. Prep.: Pil. Aloes and Mastiches.) *Kauri gum* and *amber* (succinum) occur as fossils, so does *asphaltum*. **THE OLEORESINS** are of vegetable origin and consist of mixtures in various proportions of resins with volatile oil, therefore partaking of the characters of both. They are divided into: (1) *Natural oleoresins* to which belong the turpentine, copaiba and the pitches. (2) *Prepared oleoresins*, also called *pharmaceutic oleoresins*, made by extracting oleoresinous drugs with ether or acetone. They are semi-solid preparations made from the following drugs:

aspidium, capsicum, cubeb, lupulin, pepper and ginger. *Copaiba*, commonly called "balsam of copaiba," is an oleoresin derived from various South American species of copaiba by boring holes in the heart wood. Light to brownish, viscid liquid; specific gravity, from 0.95 to 0.99, increasing with age. Soluble in absolute alcohol and the other solvents; insoluble in water. Evaporated on the water-bath, it should yield 50% residue and develop no odor of turpentine. There are four varieties of copaiba: *Rio Janeiro* and *Maranham*, containing volatile oil and resin in nearly equal amounts. The *Para* variety contains between 70 and 85% of volatile oil, while *Maracaibo* contains from 20 to 40% of volatile oils and correspondingly more resin. This last variety is the best for making the mass with magnesia, and is also preferred therapeutically, the resin being most valuable and the oil comparatively inert. *Adulteration*.—This oleoresin is frequently adulterated with *gurjun balsam*, which is detected by dropping four drops of copaiba upon a mixture of 1 c.c. of glacial acetic acid and four drops of nitric acid with which the adulterant forms a coloration. The fixed oils, like castor, cottonseed, turpentine and other oleoresins, are detected by the sticky residue on evaporating the volatile oil. Volatile oils, like turpentine and pine-needle oils, are detected by their odor when warmed. The oleoresin contains volatile oil, copaibic, oxycopaibic or metacopaibic acids, various resins and a bitter principle, soluble in water. Used as expectorant,

diuretic and stimulant in the form of the mixtures (N. F.), emulsion, paste or pill.

*The turpentine*s are oleoresins from trees belonging to the *Pinaceæ* and *Conijeræ*. All their volatile oils are terpenes. **TEREBINTHINA**, commonly called "gum," "pitch" or "common turpentine." It is a concrete oleoresin, obtained as an exudation from *Pinus palustris* and other species of pinus. Yellowish, opaque, tough masses, brittle in the cold, of terebinthinate odor and taste, contains about 30% of volatile oil and about 66% of resin. Used as diaphoretic, diuretic, stimulant and astringent; externally, in ointments and plasters. Its principal use is for the preparation of oil of turpentine by distillation, the residue being common rosin. **TEREBINTHINA CANADENSIS**, a semiliquid oleoresin obtained as an exudation from the balsam fir (*Abies balsamea*). "Canada balsam" and "balsam of fir" are two of its most common synonyms. Transparent, yellowish, viscid liquid, hardening with age, contains volatile oil and two resins. It is used as a stimulant, diaphoretic, diuretic; in ointment form for frost-bites; in microscopy as a mounting medium. The unofficial turpentine and pitches embrace the following: *Terebinthina venata* (Venice turpentine, *Terebinthina argentoratensis*, Strassburg turpentine) closely resembles Canada balsam. *Terebinthina chia* (Chian or Cyprian turpentine), appearance like balsam of fir; balsamic, fennel-like odor. **PIX BURGUNDICA** (Burgundy pitch U. S. P. '90), obtained from *Abies excelsa* or Norway spruce

fir. Semitransparent or opaque, hard, but yielding without fracture. *Pix canadensis* (hemlock pitch U. S. P. '80) resembles the previous one. *Pix liquida*, tar product of the destructive distillation of the wood of various species of pine. Viscid, blackish-brown, semifluid, with empyreumatic odor, and terebinthinate taste. Very complex composition. It contains the guaiacols and cresols. It is slightly soluble in water, more so in alcohol, fixed and volatile oils and solutions of the alkalis. Used as local stimulant and expectorant. (Preparations: Syrupus, 0.5%; Ung., 50%). From this by distillation is prepared **OIL OF TAR** (*Oleum picis liquidæ*), specific gravity, 0.97. Readily soluble, yielding acid solutions. Dose as stimulant and expectorant, 0.2 c.c. Allied to this, **OIL OF CADE** (*Oleum cadinum*), a product of the dry distillation of the wood of *Juniperus oxycedrus*. A brownish, dark liquid with a tarry odor and taste. Insoluble in water, partially in alcohol, completely in ether. Used in skin diseases.

THE BALSAMIC RESINS or "*balsams*." Balsams are oleoresins or gum-resins containing either benzoic or cinnamic acids or both. The official balsams are benzoin, peru, tolu, and styrax. Besides these, we have the balsam of the *sweet gum tree* (liquidamber styraciflua of the southern United States and the *dragon's blood* (*Resina draconis*), exudation from a palm fruit of *Dæmonorops draco*, native in Malay Archipelago. It contains both benzoic and cinnamic acids. Astringent and stimulant, employed for coloring varnishes and in plasters.

BENZOIN (benzoinum), gum benzoin. A balsamic resin obtained from *styrax benzoin*, a tree native to Sumatra, Java and Siam. It exudes from incisions made through the bark of tree. Several varieties known as the *Sumatra* benzoin, the *Siam* benzoin (having an agreeable, vanilla-like odor) and *Penang* benzoin, similar to Sumatra, more frequently resembling styrax. Benzoin contains from 12 to 20% of benzoic acid which is obtained by sublimation, cinnamic acids, various resins. Some varieties contain vanillin. Soluble in 5 parts of warm alcohol, also in solutions of the hydroxids of alkalis; insoluble in water. Antiseptic expectorant. (Preparations: Tr. Benz. 20%; Tr. Benz. Comp., 10%; Adeps Benz., 2%). When the tincture is prescribed in aqueous solutions, it should be emulsified with acacia before dispensing.

BALSAM OF PERU (*Balsamum peruvianum*), derived from *Toluifera pereiræ*. A viscid, dark brown-colored liquid, of an agreeable, vanilla-like odor and a bitter, acrid taste. Completely soluble in absolute alcohol, chloroform or glacial acetic acid. Only partially soluble in ether and petroleum benzin. Completely soluble in 5 parts alcohol, with slight opalescence. Specific gravity, 1.14 to 1.15. Contains about 60% of volatile oil; resin, 32%; cinnamic acid, benzoic acid and benzyl alcohol. Frequently adulterated with alcohol, fixed oils, copaiba, turpentine and rosin. Used in ointments internally as stimulant and expectorant, also in perfumery.

BALSAM OF TOLU (*Balsamum tolutanum*). A

balsam obtained from *Toluifera balsamum* (Central America). A yellow-brown solid, vanilla-like odor, with a mild, aromatic taste. Completely soluble in alcohol and chloroform, solutions of fixed alkalis and ether. Insoluble in carbon disulfid and benzin. Contains benzoic and cinnamic acids, two different resins, toluene and benzylic benzoate and cinnamate. Adulterated with the turpentine which, with sulfuric acid, bleaches, while the true balsam turns cherry-red. Expectorant and stimulant. Used also in perfumery. (Preparations: Tincture (20%); Syrupus and Tincture Benz. Comp.)

STYRAX, storax. A balsam prepared from the wood and inner bark of *liquidambar orientalis*, a semiliquid, grayish, sticky, opaque mass. Upon standing, separates into layers. Has an agreeable odor and a balsamic taste. Soluble in alcohol, ether and carbon disulfid. Insoluble in cold benzin, but hot benzin dissolves out the styracin and cinnamic acid, which are deposited in crystals on cooling. Composition: Benzoic and cinnamic acids, styracin, storesin, resin, etc. Used as stimulant, diuretic, expectorant (in Tr. Benz. Comp.).

GUM RESINS comprise those milky exudations of plants which contain gums, soluble in water, and resins, insoluble in water, but soluble in alcohol. Some contain volatile oils; therefore, they are divided into (1) *Those containing volatile oil*:

ASAFETIDA (asafœtida). Exudation product from *Ferula foetida* and other species of *Ferula*. Native of Afghanistan and Turkistan. Obtained

by incision. Several varieties are known, like the amygdaloid, coming in irregular pieces or tears imbedded in a sticky, brownish mass. The liquid, which is a sticky, semifluid or more or less impure mass, which darkens on exposure, and the stony variety, which contains a large proportion of calcium sulfate and other impurities. Asafetida possesses a strong, garlic-like odor, bitter acrid taste, forms a milky emulsion with water, which turns yellowish with ammonia. Asafetida should yield not less than 50% of matter soluble in alcohol. Composition: volatile oil, 3 to 9%; gum, 20 to 30%; resin, 50 to 70%, and various impurities. Stimulant, antispasmodic, expectorant. (Preparations: Emulsum, 4%; Tr., 20%; Pil. Asaf.) Usually administered in pills, suppositories or emulsion.

MYRRH (myrrha).—Spontaneous exudation from bark of *Commiphora myrrha* (Arabia). A dusty reddish or brownish mass of irregular tears; aromatic odor; bitter, acrid taste. It yields a brownish-yellow emulsion with water. Its alcoholic solution acquires a purple coloration with nitric acid. It is composed of gum, 40 to 60%; resin, 25 to 40%; a trace of volatile oil and a bitter principle. Used as a stimulant, expectorant. (Preparations: Mixt. Ferri Comp., Pil. Aloes et Myrrh, Tr. Aloes et Myrrh). Usually administered in pill or powder or as an emulsion. *The unofficial gum resins containing volatile oil are: Bdellium*, very similar to myrrh; *olibanum* (frankincense), which contains about 30% of gum, 70% of resin, with volatile oil and bitters. Used in plasters

and fumigations; *Ammoniacum*, ammoniac (spontaneous exudation product from the stem of *Dorema ammoniacum* U. S. P. '90), contains gum, 18 to 25%; resin, 70%; volatile oil, from $\frac{1}{2}$ to 4%. Used as expectorant and stimulant for making Emuls. Ammon. *Opoponax*, similar in properties and uses to ammoniac; *Galbanum*, spontaneous exudation, of which there are two kinds—the tear and lump galbanum. Its alcoholic solution, treated with HCl, turns purplish. It contains 20% of gum, 66% of resin, volatile oil, 6 to 9%. Used as antispasmodic, stimulant, expectorant.

(2) *Gum resins containing no volatile oils:* **CAMBOGIA** (gamboge), obtained by making incisions into the bark of *Garcinia hanburii* (Cochin China and Siam). Cylindrical sticks, sometimes hollow, conchoidal fracture, orange-red in color; odorless; acrid, unpleasant taste; the dust being sternutatory. Good quality yields a bright yellow powder, also bright yellow emulsion with water. Composition: gum, 16 to 20%; resin, about 80%. Used, combined with other drugs, as a hydragogue cathartic. (Preparation: Pil. Cathart. Comp.) **SCAMMONIUM** (scammony). The dried milk-juice of *Convolvulus scammonia* (Western Asia). Obtained by cutting off the top of the root and collecting the milky juice. Dark greenish or blackish, irregular masses, breaking with an angular fracture. A resinous luster; the powder has a greenish cast. With water it yields a dark greenish emulsion. Odor, cheese-like; taste, acrid. Composition: Gum, 5 to 15%; resin,

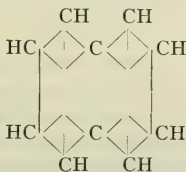
80 to 90%; frequently adulterated with starch, chalk and various resins. Used as hydragogue cathartic. (Preparation: *Resina scammonii*). Usually administered in pill form. **ELASTICA** (rubber, caoutchouc). The prepared milk-juice of *Hevea brasiliensis* and of various other species of *Hevea*. Known in commerce as Para rubber. Obtained by evaporating the milk-juice and exposing the semi-solid to fire and smoke until hard masses or "hams" are formed. Brown or brownish-black, internally lighter colored; insoluble in water, dilute acids, solutions of alkalis or alcohol; but soluble in chloroform, benzene and benzin, carbon disulfid and oil of turpentine. Lighter than water. Melting-point, 125° C., and at this temperature dissolves in petrolatum. With carbon disulfid it forms a mass used as rubber cement. The 50% solution in petrolatum with lead plaster constitutes the rubber adhesive plaster. Mixed with sulfur and heated, it is rendered insoluble and unaffected by heat, or *vulcanized* (vulcanite or ebonite or hard rubber). **EUPHORBIIUM**, an official exudation from incisions in the stem of *Euphorbia resinifera* or cactus-like shrub, is native to Morocco. It has an acrid taste, a brownish-yellow color, occurring in globular or irregular masses; not completely emulsified with water nor completely soluble in the simple organic solvents. It contains *euphorbin*, a resin, 18% of gum and impurities. Used as a violent purgative.

NAPHTHALENE AND ITS DERIVATIVES.

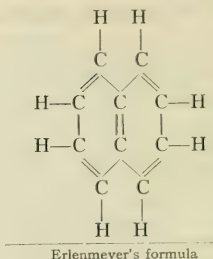
Naphthalene has the formula $C_{10}H_8$, a melting-point of $80^\circ C.$ and a boiling-point of $218^\circ C.$ It occurs in that portion of coal-tar which boils between 180 and $220^\circ C.$, and which on cooling solidifies to a mass of crystals constituting crude naphthalene. Crude naphthalene is warmed with caustic soda, to remove phenol, next with a little sulfuric acid, to remove the bases, distilled with steam, separated and dried. It is sometimes further purified by sublimation.

Properties.—Naphthalene is insoluble in water, but dissolves readily in the organic solvents. By heating it to 130° with dilute nitric acid, it is oxidized to phthalic acid; hydriodic acid will gradually reduce naphthalene to dihydrid, $C_{10}H_{10}$, tetrahydrid, $C_{10}H_{12}$, and hexahydrid, $C_{10}H_{12}$. With nascent chlorin it forms additive products: Dichlorid, $C_{10}H_8Cl_2$, tetrachlorid, $C_{10}H_8Cl_4$, etc.

Structure.—Various structural formulas were from time to time advanced for naphthalene; thus:



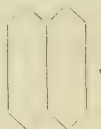
Bamberger's centric formula



Both of the above formulas have something in their favor; however, the Erlenmeyer formula, based upon Kekulé's alternate single and double bond-benzene rings, is now generally accepted.

From the Erlenmeyer's formula for naphthalin it may be regarded as two benzene rings having two carbon atoms in common.

The more compactly written formula



is now generally used in the text-books on organic chemistry. Naphthalene gives two mono-derivatives which are distinguished by the prefixes α (alpha) and β (beta). The structural formula for naphthalene shows this, on numbering the carbons in the nucleus; thus:



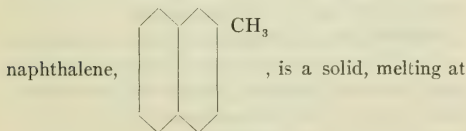
The substitution can either take place

at one of the carbon atoms which is attached to one of the two carbon atoms common to both rings; thus, 1, 4, 5 and 8, giving an *alpha* compound, while 2, 3, 6 and 7 give a *beta* compound.

Synthesis.—Naphthalene may be synthesized by passing phenylbutene bromid over red-hot lime.

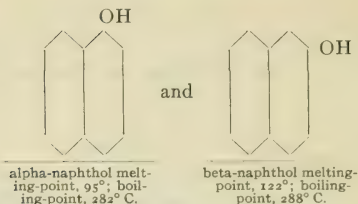


Homologues.—Two *methylnaphthalenes* and two *ethylnaphthalenes* are known. Of these β -methyl-



32°C. ; the other three compounds being liquids with high boiling-points.

When naphthalene is heated with sulfuric acid, two mono-sulfonic acids are formed. These acids, fused with caustic alkalis, similarly with the production of phenol from benzene, yield two *hydroxynaphthalenes*:



THE NAPHTHOLS are hydroxids of the monovalent radical *naphthyl*, $C_{10}H_7$, and bear the same relation to naphthalene that phenol bears to benzene.

ALPHA-NAPHTHOL, $C_{10}H_7OH$, is used as an antiseptic and antifermentative, but being more toxic is less used than—

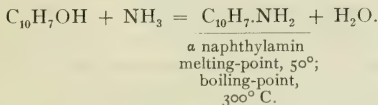
BETA-NAPHTHOL, $C_{10}H_7-OH$, is generally used as an antiseptic in cutaneous disorders as an ointment. It is soluble in aqueous solutions of alkali hydroxids, forming metallic derivatives.

ORPHOL, *Basic beta-naphthol bismuth* $(C_{10}H_7O)_3Bi + 3H_2O$, a brownish powder possessing an aromatic odor and containing about 72.5% of bismuth oxid. Used as intestinal astringent.

EPICARIN, $C_6H_3 \begin{matrix} \nearrow COOH \\ \text{---} OH \\ \searrow CH_2.O.C_{10}H_7 \end{matrix}$, is beta-naphthyl-ortho-oxymetatoluitic acid, a brownish-yellow powder, sparingly soluble in hot water, but freely in alcohol, ether and acetone. It is employed similarly to β -naphthol in skin diseases, but is said to be superior to it.

NAPHTHYLAMINS.—The two naphthylamins, $C_{10}H_7.NH_2$, resemble anilin closely and are prepared by similar methods.

ALPHA-NAPHTHYLAMIN, $C_{10}H_7.NH_2$, is obtained by heating ammonia and a naphthol with calcium chlorid to $250^{\circ} C.$:



It can also be obtained by reducing a nitronaphthalene with nascent hydrogen. It occurs in crystalline needles (Zinin, 1842).

BETA-NAPHTHYLAMIN is best obtained by acting on β -naphthol with ammonia under pressure. β -Naphthylamin melts at 112° and boils at $294^{\circ} C.$

NITRONAPHTHALENES.—By the direct nitration of α -naphthol only the *α -nitronaphthalene* is obtained. It has the melting-point $61^{\circ} C.$

The second nitro group likewise enters the alpha (1 and 4) position, consequently it is not possible to prepare *beta-nitronaphthalene* by any direct method.

Beta-nitronaphthalene is obtained from β -naphthylamin by the diazo-reaction. It melts at $79^{\circ} C.$

NAPHTHALENE SULFONIC ACIDS, $C_{10}H_7.SO_3H$, are formed when naphthalene is heated with strong sulfuric acid. The ordinary naphthalene sulfonic acid is a mixture of both the alpha and beta varieties. These vary in ratio to each other with the temper-

ature of the reaction; thus: At a temperature not exceeding 80° mostly the *alpha* is formed, while at 160° C. the *beta* acid predominates.

When fused with potash, these acids are decomposed into the corresponding naphthols.

NAPHTHYLAMIN SULFONIC ACIDS are employed in the manufacture of such azo dyes as *congo red*—*benzopurpurin*, etc.

NAPHTHIONIC ACID (1 and 4) is obtained by heating in vacuo α -naphthylamin sulfate to 130° C.; it has the formula $C_{10}H_6(NH_2)SO_3H$.

MARTINS' YELLOW is obtained by acting with strong nitric acid upon α -naphthol. The sodium salt, $C_{10}H_5(OH)_2ONa, H_2O$, is used as a dye.

NAPHTHOL YELLOW is obtained by acting with strong nitric acid upon α -naphthol-trisulfonic acid. The potassium salt is used as a dye.

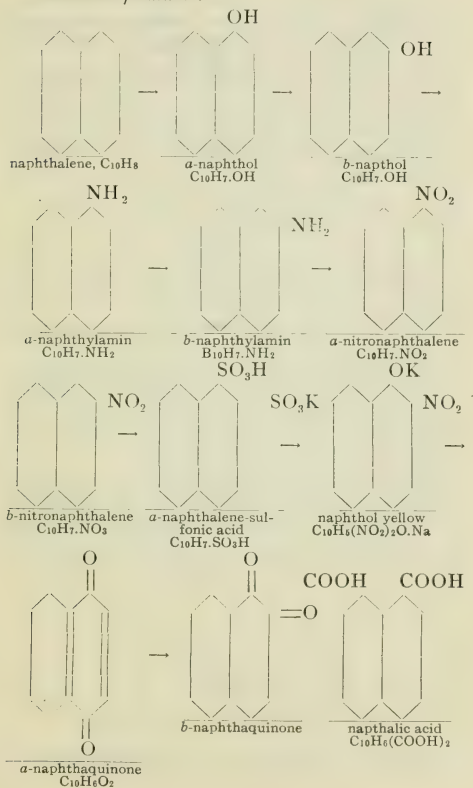
NAPHTHAQUINONES.—Two isomers are known, of which α -naphthaquinone corresponds to benzoquinone in properties. Their formula is $C_{10}H_6O_2$.

NAPHTHOIC ACIDS.—Naphthalene forms also the unimportant carboxylic acids, of which the two known ones will be given:

α -**NAPHTHOIC ACID**, $C_{10}H_7\cdot COOH$, obtained by the hydrolysis of the α -cyanid $C_{10}H_7\cdot CN$; melts at 160° C.

β -**NAPHTHOIC ACID**, prepared from the β -cyanid; melts at 182° C.

NAPHTHALIC ACID, $C_{10}H_6(COOH)_2$, has the two carboxyls in *periposition* (both in *alpha* 1, 8).

Structural formulas:

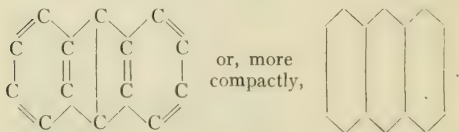
ANTHRACENE.—

Anthracene, $C_{14}H_{10}$, occurs in that fraction of the heavy coal-tar oil which boils between 230° and 270° C. It is found as a light brown deposit, mixed with *phenanthrene* and *carbazole*. This sediment is separated by means of a filter press and the residue is washed free from oil, with naphtha. The product contains, and is known in commerce as, "50 per cent." anthracene. From this crude anthracene *alizarin* and other valuable dyes are made.

By mixing the crude anthracene with solid potassium hydroxid, it combines with carbazole, forming *potassium carbazole*, and the residue with carbon disulphid, with which phenanthrene (more soluble) can be washed out.

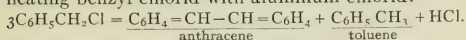
Properties.—Anthracene occurs in colorless plates, having a bluish fluorescence, melting at 213° and boiling at 351° C. It is insoluble in water, but readily soluble in the organic solvents.

Structure.—Naphthalene is frequently regarded as a condensation of two benzene rings with the loss of two carbon atoms; just so, anthracene may be regarded as a condensation of three benzene-rings with the loss of four carbon atoms:

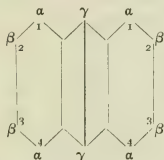


Synthesis.—Anthracene may be synthesized by

passing petroleum through red-hot tubes; also by heating benzyl chlorid with aluminum chlorid:



SUBSTITUTION PRODUCTS.—Three isomeric monosubstitution products of anthracene are possible; these can be distinguished by prefixing their names with the Greek letters α , β or γ :



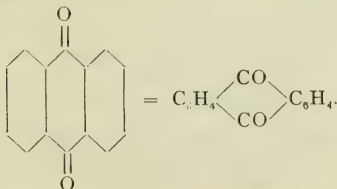
also fifteen disubstitution products.

ANTHRAQUINONE.—With the exception of anthraquinone and its hydroxids, the products of anthraquinone are of little pharmaceutic importance.

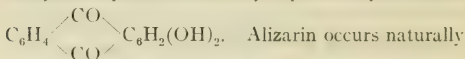
Anthraquinone, $\text{C}_{14}\text{H}_8\text{O}_2$, is prepared by oxidizing anthracene with chromic acid. It occurs in yellow, insoluble prisms, which dissolve in benzene; melt at 285°C ., and at higher temperatures sublime.

With hydriodic acid it is reduced to anthracene.

Structure:

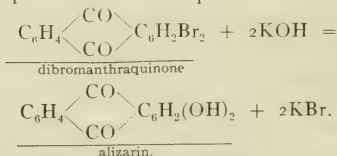


HYDROXYANTHRAQUINONES.—The α - β -*dihydroxyanthraquinone* is the very important dye *alizarin*,

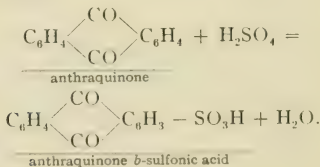


in the *madder root* (*Rubia tinctoria*) as ruberythric acid, and has from early times been employed as a red dye-stuff. Alizarin is one of the most important dyes in the entire galaxy of dyes. It is also one of the most important synthetic economic discoveries (Perkin, Graebe and Liebermann, 1868) of all the times.

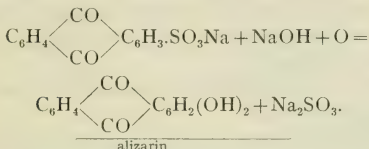
It was originally synthesized by fusing dibromanthraquinone with caustic potash:



Synthesis.—The above method, proving too costly, was later relinquished for another process, consisting in the heating of anthraquinone with pyrosulfuric acid to 160°C . and forming *anthraquinone-beta-sulfonic acid*:



This acid is neutralized with sodium carbonate and the so-formed sodium salt is fused with caustic soda and a little potassium chlorate, the chlorate furnishing the necessary oxygen:



The alizarin formed is dissolved out in water, digested with milk of lime, and insoluble calcium alizarate is filtered out. This calcium salt is next decomposed with hydrochloric acid, whereupon the alizarin precipitates as a brown, amorphous powder. It is sent into commerce as a 10 or 20% *alizarin paste*.

Properties.—Alizarin is insoluble in water, but dissolves in the caustic alkalis with a violet color, forming corresponding alkali salts. This violet color is bluer in the presence of NaOH, and redder if NH₄OH is present.

With the metallic compounds it forms insoluble compounds of different colors, called "lakes;" thus, with the ferric salts a "violet lake"; with chromium salts, "brown lakes"; with aluminum salts, "bright red lakes"; with barium chlorid, "deep purple lake"; with stannous chlorid, "orange lake." These alizarates can be precipitated with ammonium hydroxid, collected, dried and used as pigments; thus, with aluminum acetate the familiar *turkey-red* is obtained.

In 1880, \$8,000,000 worth of alizarin had been made artificially. Had this same amount of alizarin been made from madder root, the cost of the necessary material alone, irrespective of labor, would have been \$28,000,000. Thus a saving of \$20,000,000 had been effected in one year by one synthetic chemical method.

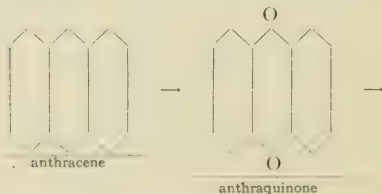
Alizarin orange and *alizarin blue* are some of the alizarin derivatives.

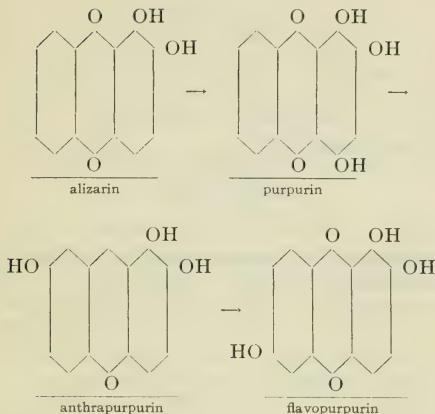
PURPURIN (1, 2, 4), *trihydroxyanthraquinone*, occurs, like alizarin, in the roots of the various species of *rubia*, and it can be obtained from alizarin by heating it with manganese dioxid and sulfuric acid. It occurs in yellowish-red, slightly hot-water-soluble prisms. In the presence of *mordants*, it dyes fabrics a yellowish-red color.

ANTHRAPURPURIN (1, 2, 2'), *trihydroxyanthraquinone*, is obtained by fusing 1,2' disulfonic acid with caustic soda and potassium chlorate.

FLAVOPURPURIN (1, 2, 3'), *trihydroxyanthraquinone*, is formed in a similar way to anthrapurpurin from 1, 3' anthraquinone sulfonic acid.

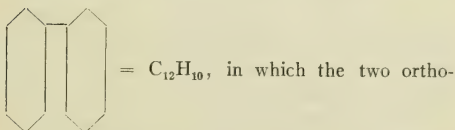
Structure:



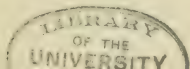


PHENANTHRENE, $C_{10}H_{14}$, is isomeric with anthracene, and is found in coal-tar associated with it. It occurs in colorless needles, melting at 99° and distilling at $340^{\circ} C$.

Phenanthrene is regarded chemically as diphenyl



positions are linked by the group $-CH=CH-$; thus:



CHAPTER XXXVII.

HOMOCYCLIC AND HETERO-CYCLIC SUBSTANCES.

ALL the ring (cyclic) structures thus far studied have been composed of *similar atoms*, namely, carbon. Thus, benzene, naphthalene, anthracene, have only carbon in their rings; such substances are called *homocyclic*.

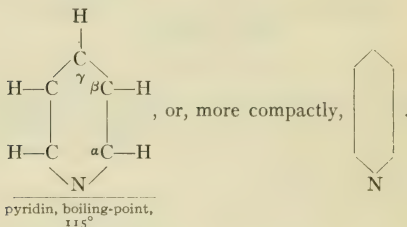
There are known, however, compounds having two or more *dissimilar atoms* in their rings, these are known as *heterocyclic* substances. An important example of this latter class is had in *pyridin*, C_5H_5N .

PYRIDIN, C_5H_5N , is a colorless liquid with an odor like tobacco smoke and a boiling-point of $115^{\circ} C$.

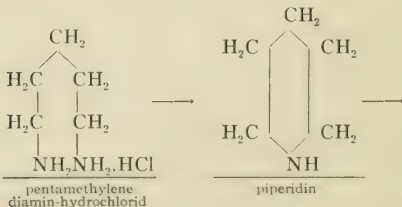
Pyridin occurs in bone oil, "Dippel's oil," produced by the destructive distillation of bones. The fraction passing at 150° is collected and converted into pyridin ferrocyanid, which is purified by recrystallization and decomposed by the alkalis. Pyridin is soluble in water. When treated with metallic sodium in an alcoholic solution, it is converted into piperidin, $C_5H_{11}N$.

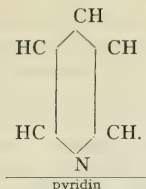
With the halogens it forms substitution products, and under certain conditions also addition products.

With acids pyridin forms stable crystallizable salts by addition, thus proving its amin nature. It is not acted upon by nitrous acid, nor is it converted into *isonitril* by alcoholic potash and chloroform, proving that it is a tertiary amin, having the structure



This structure is verified by its synthesis from penta-methylene-diamin hydrochlorid. By rapidly heating this latter salt, it loses one molecule of NH_4Cl , becoming converted into *piperidin*, the hexahydrid of pyridin. This, by mild oxidation, is converted to pyridin:





Regarding the situation of the carbon atoms to the nitrogen atom, it is apparent that it should form three isomeric mono-substitution products, and in reality three such isomerids are known in the three pyridincarboxy acids; thus:

(α) picolinic acid (β) nicotinic acid (γ) isonicotinic acid.
COOH.

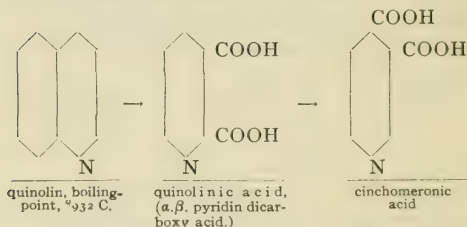


Pyridin has several homologues: The methyl pyridins, known as *picolins*; dimethylpyridins, known as *lutidins*; and trimethylpyridins, known as *collidenes*.

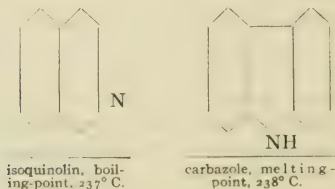
QUINOLIN, C_9H_7N (Gerhardt, 1842), like pyridin, occurs in bone oil and coal-tar oil. It can be synthesized by boiling together a mixture of anilin, nitrobenzene, glycerol and sulfuric acid, removing the undecomposed nitrobenzene by steam, rendering alkaline and separating the quinolin with a current of steam.

Quinolin is a colorless oil with an unpleasant penetrating odor, sparingly soluble in water and boiling at 239°C . It combines, like pyridin, with the acids, and exhibits all the other properties of tertiary amins.

Upon oxidation, quinolin is first converted into tetra- and finally into decahydroquinolin. With potassium permanganate it is oxidized into quinolinic acid.



ISOQUINOLIN, $\text{C}_9\text{H}_7\text{N}$, occurs, like quinolin, in bone oil (Hoogewerff). It was first obtained from crude quinolin by fractional crystallization of the sulfate. It occurs in crystals, melting at 21° and boiling at 237°C .



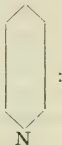
CARBAZOLE, $C_{12}H_9N$, occurs with anthracene in anthracene grease. Melting-point, 238° ; boiling-point, 351° C.

THE ALKALOIDS.

Some of the basic substances already mentioned, as pyridin, quinolin and isoquinolin, are usually considered as the simpler alkaloids.

Alkaloids are now frequently classified with reference to their parent body; *i. e.*, body of which they are considered derivatives; thus:

DERIVATIVES OF PYRIDIN,



:

Lobeline, $C_{16}H_{24}NO$, from Indian tobacco (*Lobelia inflata*).

Sparteine, $C_{15}H_{26}N_2$, from broom (*scoparius*).

Piperidine, $C_5H_{11}N$, found in pepper (*Piper nigrum*).

Coniine, $C_8H_{17}N$, found in poison hemlock (*Conium maculatum*), a liquid alkaloid, boiling at 167° C.

Nicotine, $C_{10}H_{14}N_2$, from tobacco (0.6 to 8%) (*Nicotiana tabacum*).

Piperine, $C_{17}H_{19}NO_3$, found in pepper (8%).

Atropine, $C_{17}H_{23}NO_3$, found in belladonna (*Atropa belladonna*), thorn-apple (*Datura stramonium*), henbane (*Hyoscyamus niger*). It melts at 115° C.

Hyoscyamine, $C_{17}H_{23}NO_3$, found associated with

scopolamine in the plants of the deadly nightshade family. It melts at 108.5° C., and at this temperature becomes converted into the isomeric alkaloid atropine.

Scopolamine, found in the plants of the "deadly nightshade" family and purported to constitute the bulk of the hyoscine of commerce, with which it is said to be identical. This last statement should be treated with some skepticism until more is known of the structure of these alkaloids; scopolamine melts at 198° C.

Hyoscine, $C_{17}H_{21}NO_4$, found in the plants of the deadly nightshade family.

Homatropine, $C_{16}H_{21}NO_3$, an artificial alkaloid—tropine mandelate.

The last-mentioned five alkaloids constitute the class of "mydriatic alkaloids," capable of dilating the pupil of the eye. Homatropine is deemed the most desirable, since its mydriasis wears off in twenty-four hours.

Cocaine, $C_{17}H_{21}NO_4$, occurs associated with eight closely related alkaloids in coca leaves (*Erythroxylon coca*). Cocaine also exerts a slight mydriatic action, but is chiefly employed as a local anesthetic. It melts at 98° C.

DERIVATIVES OF QUINOLIN,



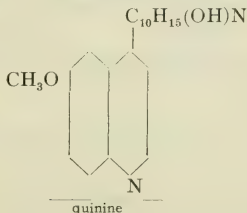
Quinine, $C_{20}H_{24}N_2O_2$, found with other alkaloids in cinchona bark (*Cinchona calisaya*) and other varieties of cinchona (8 to 10%). It is a diatomic base and forms two classes of salts; melts at $177^\circ C$.

Cinchonine, $C_{19}H_{22}N_2O$, found associated with quinine (2.5%). It is, like quinine, dibasic and forms two classes of salts; it melts at $250^\circ C$.

Quinidine and *cinchonidine* are two other alkaloids of cinchona, distinguished from the former two by being *dextrogyrate* and forming *soluble tartrates*.

Quinine and cinchonine are *levogyrate*; and form *sparingly soluble tartrates*. To detect whether quinine or its salts are contaminated with the *cheaper* cinchona alkaloids, it should *readily dissolve* in *ammonia water*; the other alkaloids do not.

Structure:



Morphine, $C_{17}H_{19}NO_3 \cdot H_2O$, found in opium (from *Papaver somniferum*) together with twenty other alkaloids, as follows; morphine, 10%; narcotine, 6%; papaverine, 1%; codeine, 0.5%; thebaine, 0.3%; narceine, 0.2%, etc.; separated by Sertürner.

It melts at 230° , and is a strong narcotic.

Codeine, $C_{18}H_{21}NO_3$, is a homologue of morphine,

and found associated with it. It melts at 153°C . and is the most soluble of opium alkaloids.

Strychnine, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$, found in the "dog-button" (*Strychnos nux vomica*) and other *strychnos* species. It melts at 284° , is a monacid base; sparingly soluble in water, readily in the acids. Very strongly poisonous, producing tetanus even in small doses.

Brucine, $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$, crystallizes in colorless prisms and melts at 178°C . Sparingly soluble, monacid base.

Colchicine, $\text{C}_{21}\text{H}_{22}(\text{CH}_3\text{O})\text{NO}_5$, found in *Colchicum autumnale*. Amorphous alkaloid, melting at 147°C . When hydrolyzed, it yields a second alkaloid, *colchicinein*, $\text{C}_{21}\text{H}_{22}\text{OHNO}_5$.

Physostigmine, $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_2$, also called *eserin*; found in calabar bean (*Physostigma venenosum*). While the alkaloids of the *deadly nightshade* family are all *mydriatic*, the opium alkaloids are all *myotic* (contracting the pupil of the eye); but the strongest myotic is found in *physostigmine*.

Pilocarpine, $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$, found in jaborandi leaves (*pilocarpus*). It is a deliquescent alkaloid, very soluble, used to produce diaphoresis.

Veratrine, $\text{C}_{37}\text{H}_{53}\text{NO}_{11}$, found in *cevadilla* seed (*Asagrea officinalis*), and not from *veratrum*, as is erroneously supposed. It is poisonous and a powerful sternutatory.

THE DERIVATIVES OF XANTHIN have been considered on page 392, and embrace *theine*, *caffeine* which is official as well as its mixture with citric acid (50% each), the "citrated" *caffein*, *guanine*,

kolanine and *theobromine*. The salicylate of theobromine is employed as a diuretic under the name of *Diuretin*.

DERIVATIVES OF PYRROL, $C_4H_4:NH$; pyrrol is found in bone oil (Dippel's oil) together with

pyridin. It has the structural formula, $\begin{array}{c} HC-CH \\ || \quad || \\ HC \quad CH: \\ \diagdown \quad \diagup \\ NH \end{array}$

Iodol, C_4I_4NH , is produced by acting with iodine and caustic potash on pyrrol. It is a brown, odorless powder containing about 89% of iodine, and used as a substitute for iodoform.

Pyrazol, $C_3H_4N_2$, has been obtained artificially from hydrazine and chlorhydrin. Its structural

formula is $\begin{array}{c} CH-CH \\ || \quad || \\ N \quad CH \\ \diagdown \quad \diagup \\ NH \end{array}$ and the melting-point, $70^\circ C$.

Antipyrin, $C_{11}H_{12}N_2O$, *phenazone*, is an artificial alkaloid made from phenylhydrazine and acetoacetic ester. By heating these, condensation occurs and a ketone, phenylmethyl pyrazolone, is formed. This ketone, heated with methyl iodide and potassium

hydroxide, yields antipyrin, $\begin{array}{c} CH_3.C=CH \\ | \quad | \\ CH_3.N \quad CO \\ \diagdown \quad \diagup \\ N-C_6H_5 \end{array}$, soluble

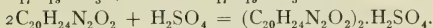
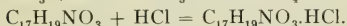
antipyrin, melting-point, $113^\circ C$.

and a *very incompatible* febrifuge.

DEFINITION AND DISCUSSION.

The alkaloids may be considered as basic carbonaceous amins which combine with acids similarly to ammonia to form crystalline salts. There are *vegetable alkaloids*, like morphine; *animal*, as ptomain, and *artificial alkaloids*, as quinolin. They are the most powerful of the organic principles. They all contain, in addition to nitrogen, C and H and, with few exceptions, O. When heated with alkalis, ammonia is given off (distinction from glucosids). Alkaloids are usually named after the generic name of the drug. The suffix "ine" (Latin, "ina") distinguishes them from glucosids and other principles. Some alkaloids, like morphine, which has been named in honor of Morpheus (the god of sleep), and the alkaloids of the cinchonas are named arbitrarily; thus, pelletierine has been named after the discoverer, etc. They may be divided into *amins* and *amids*; the *amids* containing oxygen, the *amins* not containing it. The *amins* are liquid and volatile alkaloids and embrace coniine, sparteine, nicotine, lobeline, while all the *amids* are solid bodies. They are all insoluble in water, but soluble in alcohol, chloroform, benzin, benzol, amylic alcohol, kerosene, and some in ether. They do not exist naturally in the free state, but as acids or neutral salts combined with some acids peculiar to the plants; thus, as quinine and cinchonine, combined with the kinic acid peculiar to cinchona. The opium alkaloids are combined with meconic acid, as meconates and the

strychnos alkaloids of nux vomica, etc., combined with igasuric acid, while other alkaloids are combined with such common acids as tannic, citric, tartaric, etc. *Alkaloidal salts*: when forming salts, the alkaloids do not replace the hydrogen of acids, thus showing the terms "sulfate," "chlorid," etc., to be incorrect when applied to an alkaloidal salt. They should be named "hydrosulfate," "hydrochlorid," respectively, etc. Ammonia hydrochlorid (ammonium chlorid) may serve as a type of the formation of alkaloidal salts; thus:



GENERAL METHODS OF EXTRACTION.—(1)

When the native alkaloidal salt is soluble in water and the alkaloid itself insoluble, strong alkali is added to a decoction of the vegetable substance. It neutralizes the organic acid with which the alkaloid is associated, precipitating the alkaloid in an impure state. (2) When the native alkaloidal salt is insoluble in water, a very dilute acid is used in the extraction of the drug, so that it combines with an inorganic acid to form a salt. This solution is decomposed with an alkali, yielding the alkaloid as a precipitated salt. The process may be divided into six steps; thus: (1) Solution; (2) precipitation; (3) re-solution; (4) decolorization (with animal charcoal or lime); (5) purification; (6) crystallization. *The salts of the alkaloids* are soluble in water, some

are very freely soluble in alcohol, but most of them are insoluble in ether and chloroform.

Tests.—(1) Phosphomolybdic acid (Sonnenschein's Reagent) produces yellow precipitate. (2) Nitric and sulfuric acids color many alkaloids reddish. (3) Sodium phosphotungstate (Schiebler's) produces precipitates soluble only in H_3PO_4 . (4) Potassium mercuric iodid (Mayer's) forms yellowish precipitates insoluble in acidulated aqueous solutions. (5) Cadmium potassium iodids (Marme's) gives a gelatinous precipitate. Other alkaloidal precipitants are picric acid and the following chlorids: Hg, Pt, Au, Sn, lead acetate and subacetate, Lugol's solution, KI and the iodids of Hg, Bi and Zn. With tannin insoluble tannates are formed (antidote).

Among the unofficial alkaloids, aspidospermine, from quebracho bark; berberine, from berberis and hydrastis; coniine, from conium seed; delphinine, from staphisagria; emetine and cephæline from ipecac; gelsemine, from yellow jasmine, and jervine and veratrabine, from veratrum (white and green), may be mentioned.

THE ANIMAL ALKALOIDS, PTOMAINS AND LEUKOMAINS.—The ptomains, as the cadaveric alkaloids are called, were so named by Selmi in 1870. This authority demonstrated that such changes as *putrefaction*, fermentation, etc., of the albuminous bodies are productive of alkaloid-like bodies; that these may be either liquid or solid, volatile or fixed.

PTOMAINS are formed by the putrefactive changes

PHARMACOPOEIAL ALKALOIDS AND THEIR SALTS.

Official Title.	Formula.	Solubilities, 25° C.			Average dose.
		Water.	Alc.	Eth.	
Cinchona alkaloids.	Quina,	$C_{20}H_{24}N_2O_2 + 3H_2O$	1750	0.6	1.9
	Quinine sulphas,	$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 7H_2O$	720	86	400
	Quinine bisulphas,	$C_{20}H_{24}N_2O_2H_2SO_4 + 7H_2O$	8.5	18	920
	Quinine hydrochloridum,	$C_{20}H_{24}N_2O_2HCl + 2H_2O$	18	0.6	0.8
	Quinine hydrobromidum,	$C_{20}H_{24}N_2O_2HBr + H_2O$	40	7	very
	Quinine salicylas,	$C_{20}H_{24}N_2O_2C_7H_6O_3 + H_2O$	77	11	37
	Cinchonine sulphas,	$(C_{19}H_{22}N_2O)_2H_2SO_4 + 2H_2O$	58	10	69
	Cinchonidine sulphas,	$(C_{10}H_{22}N_2O)_2H_2SO_4 + 3H_2O$	63	72	900
	Morphina,	$C_{17}H_{19}NO_3 + H_2O$	3330	168	1800
	Morphine sulphas,	$(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$	15.3	465	Ins.
Opium alkaloids.	Morphine hydrochloridum,	$C_{17}H_{19}NO_3HCl + 3H_2O$	17.2	42	Ins.
	Morphine acetat,	$C_{17}H_{19}NO_3 \cdot C_2H_4O_2 + 3H_2O$	2.25	21.6	480
	Apomorphine hydrochloridum,	$C_{17}H_{17}NO_2HCl$	45	45	3800
	Codeina,	$C_{18}H_{21}NO_3 + H_2O$	88	1.6	0.66
Nuxvomica alkaloids.	Codeine phosphas,	$(C_{18}H_{21}NO_3)_3H_3PO_4 + 2H_2O$	2.5	261	6620
	Codeine sulphas,	$(C_{18}H_{21}NO_3)_3H_2SO_4 + 5H_2O$	30	1035	Ins.
	Strychnina,	$C_{21}H_{22}N_2O_2$	6400	110	6
	Strychnine sulphas,	$(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 5H_2O$	31	65	225
	Strychnine nitras,	$C_{21}H_{22}N_2O_2HNO_3$	42	120	136

PHARMACOPOEIAL ALKALOIDS AND THEIR SALTS.—Continued.

Official Title.	Formula.	Solubilities, 25° C.				Average dose.
		Water.	Alc.	Eth.	Chlor.	
Atropina, Atropinæ sulphas, Hyoscyaminæ sulphas, Hyoscyaminæ hydrobromidum, Hyoscinæ hydrobromidum, Homatropinæ hydrobromidum, Scopolaminæ hydrobromidum.	$C_{17}H_{23}NO_3$ $(C_{17}H_{23}NO_3)_2H_2SO_4$ $(C_{17}H_{23}NO_3)_2H_2SO_4$ $C_{17}H_{23}NO_3HBr$ $C_{17}H_{21}NO_4HBr + 3H_2O$ $C_{16}H_{21}NO_3HBr$	430 0.38 0.5	1.46 3.7 6.4	16.6 2140 2500	1.56 620 2300	0.0004 0.0004 0.0005
	Chemically claimed identical with hyoscine hydrobromid.					
Aconitina, Caffeina, Cocaina, Cocainæ hydrochloridum, Colchicina, Hydrastina, Hydrastinæ hydrochloridum, Physostigminæ sulphas, Physostigminæ salicylas, Pilocarpinæ hydrochloridum, Pilocarpinæ nitras, Sparteina sulphas,	$C_{34}H_{47}NO_{11}$ $C_8H_{10}N_4O_2 + H_2O$ $C_{17}H_{21}NO_4$ $C_{17}H_{21}NO_4HCl$ $C_{22}H_{25}NO_6$ $C_{21}H_{21}NO_6$ $C_{11}H_{11}NO_2HCl$ $(C_{16}H_{21}N_3O_2)_2H_2SO_4$ $C_{15}H_{21}N_3O_2C_7H_6O_3$ $C_{11}H_{16}N_2O_2HCl$ $C_{11}H_{16}N_2O_2HNO_3$ $C_{15}H_{26}N_2H_2SO_4 + 5H_2O$	3200 45.6 600 0.4 22 Ins. very very 72.5 0.3 4 1.1	22 53.2 5 2.6 very 135 very very 12.6 2.3 60 2.4	44 375 3.8 Ins. 155 124 1300 1200 175 Ins. Ins. Ins.	very 8 very 18.5 very 2 286 very 8.6 540 Ins. Ins. Ins.	1.15mg. 0.005 0.03 0.03 0.5 mg. 0.01 0.03 0.001 0.001 0.01 0.01 0.01

Mydriatic alkaloids.

of the animal tissues, and may be harmless or poisonous. Among the *nonoxygenated* liquid *ptomains*, the following are monamins: dimethylamin, triethylamin and propylamin. Among the diamins: tetra-methylene-diamin (*putrescin*), $C_4H_{12}N_2$; penta-methylene-diamin (*cadaverin*), $C_5H_{14}N_2$, and its isomer found in decomposing flesh—*neuridin*.

Hydrocollidin, $C_{11}H_{13}N$, is found in decomposing horse-flesh.

Collidin, $C_8H_{11}N$ (trimethyl-pyridin), and the tetramethyl-pyridin (*parvolin*), $C_9H_{13}N$, are also important.

The *oxygenated ptomains* of importance, besides the already-described *neurin* and *cholin*, are:

Gadinin, $C_7H_{16}NO_2$, found in putrid fish; *myli-toxin* $C_6H_5.NO_2$, found in poisonous mussels. Gautier (1880) announced that in the animal excreta poisonous alkaloids are found, and he named these "leukomains."

LEUKOMAINS are basic substances formed by the retrograde metamorphosis in the human body. Leukomains include the xanthin bases; some are poisonous, some not.

TOXINS are classed as ptomains, formed by the action of the pathogenic bacteria in the living body.

The combined action of the above *three* classes of products has a deleterious effect on the human body, known as *autointoxication*. Autointoxication, therefore, is due to the incomplete oxidation and excretion of these accumulated products in the system.

ANTITOXINS are bodies found in the blood-serum, which have been developed there by the action of certain microorganisms in the body. They have the property of protecting the animal system against further infection by the same organism. This protection is known as *immunity*.

THE PROTEINS.

The proteins form the chief and constant organic constituents of the animal and, to a certain extent, plant bodies.

Their composition is very complex and their structure unknown; they all contain carbon, oxygen, hydrogen, nitrogen, sulfur and phosphorus, and some contain iron.

Proteins are amorphous, nonvolatile, nondiffusible, odorless, colorless and tasteless bodies. On destructive distillation, they yield ammoniacal derivatives.

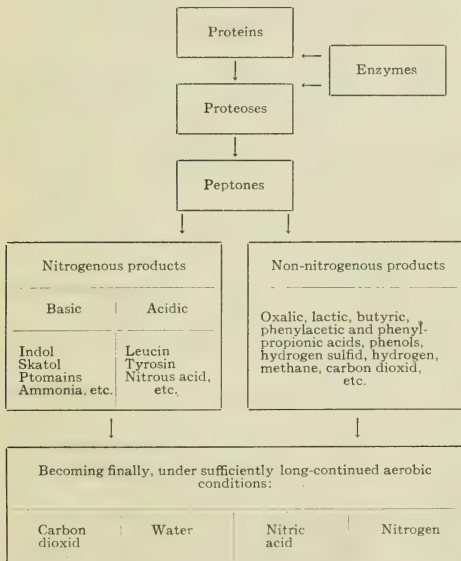
When warmed *with nitric acid*, their aqueous solutions are *colored yellow* (*xanthoproteic reaction*); heated *with mercuric nitrate* in a solution of nitric acid, proteins turn *red* (*Millon's reaction*); boiled *with sodium hydroxid* solutions, upon the addition of a little *cupric sulfate* solution, proteins give *violet-pink* color (*Biuret reaction*); boiled *with glacial acetic acid*, and underlayered with strong H_2SO_4 , proteins give a *purple color* at line of contact (*Adamkiewicz's reaction*).

Gelatin and *peptone* are examples of the *proteins*. They are all distinguished by the ease with which they undergo *putrefaction*.

PUTREFACTION.

Putrefaction is a fermentative change taking place in nitrogenous substances:

Example (Meeker):



CHAPTER XXXVIII.

THE TERPENES AND ESSENTIAL OILS.

THE terpenes are volatile proximate principles of plants. Common oil of turpentine is the commonest type of the terpenes. Terpenes are hydrocarbons having an empiric formula, $(C_5H_8)_n$. The following groups of terpenes are distinguished:

1. *Hemiterpenes*, C_5H_8 . Example: isoprene in rubber.

2. *Terpenes*, $C_{10}H_{16}$. Example: australene in turpentine oil.

3. *Sesquiterpenes*, $C_{15}H_{24}$. Examples: *cadinene* and *gubebin*.

4. *Diterpenes*, $C_{20}H_{32}$. Example: *Colophene*—oxygenated turpentine.

5. *Polyterpenes*, $(C_{10}H_{16})_n$. Examples: *caoutchouc* and *gutta-percha*.

The *terpenes* are further subdivided into *three classes*, according to physical and chemical properties.

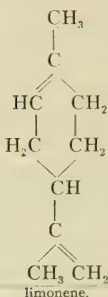
(1) **PINENE CLASS.**—This class embraces the colorless terpenes, having agreeable odors, boiling about 156° , and having specific gravities about 0.8. They are usually optically active; when treated with dry hydrochloric, hydrobromic or hydriodic acid, they *add* on one molecule of these acids. Thus is obtained *pinene hydrochlorid*, $C_{10}H_{16}.HCl$, known

as "artificial camphor." With bromin they form dibromids, and with nitrosyl chlorid, crystalline compounds; with iodin and sulfuric acid, pinene is converted into *cymene*.

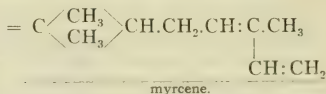
It occurs in varying quantities in many essential oils; the dextro-modification, *australene*, is found in the American turpentine (*Pinus australis*), while the levo-modification, *terebenthene*, is found in the French turpentine (*Pinus maritima*). It boils at 155° C., and has the specific gravity 0.855, and is obtained by distilling turpentine resin (gum) with steam.

Turpentine oil (*Oleum terebinthinæ*) is employed in the manufacture of paints and varnishes. It absorbs oxygen, in time becoming resinified. It fulminates when mixed with iodin.

(2) **LIMONENE CLASS.**—Members of this group are also colorless, very aromatic liquids, boiling at about 170° , having the specific gravity 0.8. These combine with *two molecules* of dry hydrochloric-acid gas, forming *dihydrochlorids*, while with bromin they form crystalline *tetrabromids*. Oil of lemon peel and *phellandrene*, occurring in certain eucalyptus oils, lime and citron oils, are types of the limonenes. They are optically active. Limonene is also called *citrene*, *carvene* and *hesperidene*. Both the *pinenes* and *limonenes* are *cyclic compounds*:



(3) **MYRCENE CLASS.**—But few of the myrcenes known. The chief difference between this and the above two classes lies in the fact that the myrcenes are unsaturated, open-chain hydrocarbons,



Myrcene is a constituent of bay oil, which is the class representative.

Dipentene is the racemic (inactive) form of the pinenes. It is found in many essential oils and in turpentine, and can be made by mixing equal parts of the two active limonenes.

SESQUITERPENES, $\text{C}_{15}\text{H}_{24}$, are the higher polymers of hemiterpenes and constitute an interesting group of terpenes. In that, some are cyclic and others not, some form additive products with HCl gas, others will not. *Cadinene*, from oil of cade;

humulene, from hop oil, constitute the reactive examples of the group, while *clovene* and *caryophyllene*, both from clove oil, are nonreactive examples.

When oil of turpentine is exposed to the action of the air in the presence of alcohol and nitric acid, a crystalline compound, known as *terpin hydrate*, $C_{10}H_{18}(OH)_2 \cdot H_2O$ (terpini hydras U. S. P.), deposits through the union of three molecules of water. It occurs in rhombic prisms, melting at $116^{\circ}C$. Terpene hydrate, upon boiling with dilute sulfuric acid, loses two molecules of water and is converted into *terpineol*, $C_{10}H_{17}OH$, known as synthetic *lilac* or *syringa* oil, extensively used in perfumery. Allowed to stand 24 hours in contact with sulfuric acid, turpentine becomes converted into *terebene* (terebenum U. S. P.). Terebene is an optically inactive mixture of dipentene, terpinene, cymene and camphene. It boils, when pure, at 170° to $185^{\circ}C$.

Terpinene is an isomer of limonene, and so is *terpinolene*.

Camphene can be obtained by saponification of pinene hydrochlorid. Camphene is a crystalline body melting at $49^{\circ}C$. When *turpentine* is subjected to distillation, the volatile portion which passes over with steam constitutes the turpentine oil, while the transparent amber-colored residue constitutes *colophony* or "rosin." This rosin consists mainly of a complex acid which is a derivative of phenanthrene, and called *abietic acid*, $C_{18}H_{27}COOH$. It melts at $146^{\circ}C$., dissolves entirely in caustic alkalis, constituting the "rosin soap" of commerce.

POLYTERPENES, $(C_{10}H_{16})_n$. These can be obtained by polymerizing turpentine oil with antimonyl chlorid. The most important are the class of rubbers.

CAOUTCHOUC is contained in the sap of the India-rubber tree, (*Hevea elastica*). This milky sap hardens on exposure and constitutes "India rubber," specific gravity, 0.96. It vulcanizes with sulfur chlorid, constituting "vulcanite," *ebonite*, used for many useful purposes. The best variety of *caoutchouc* is *para* rubber (*elastica* U. S. P.).

GUTTA-PERCHA.—The coagulated milky juice of *dichopsis* trees (*Isonandra gutta*). Specific gravity, 0.98. It is decomposed on melting. Nonelastic below 60° , but very soft at 100° C. It is soluble in benzol, chloroform, turpentine and carbon disulfid, with which it forms the *rubber cement*.

Balata and *chicle* gums resemble gutta-percha closely.

OXYGENATED CONSTITUENTS OF THE ESSENTIAL OILS.

While the various terpenes usually constitute the bulk (body) of the essential oils, their odors are due to some of the *oxygenated carbon* compounds, namely:

Alcohols: Borneol, linalool, geraniol, citronellol, santalol, menthol, cineol.

Esters: Bornyl acetate and other borneol esters; linalool esters, like the acetate; geraniol esters, like the acetate; methyl esters, like the salicylate.

Aldehyds: Citral (geranial), citronellal; benzoic and cinnamic.

Ketones: Menthone; carvone, methyl nonyl ketone and camphor.

Phenols: Thymol, eugenol, carvacrol.

CAMPHOR, $C_{10}H_{16}O$, is obtained by boiling chips of wood from the camphor-tree (*Cinnamomum camphora*) in a vessel with a perforated dome into which the camphor sublimes. Camphor (camphora U. S. P.) is defined as the dextrogyrate modification of the saturated ketone obtained by sublimation from camphor wood *Cinnamomum c.* It has a characteristic odor, cooling taste and melts at $175^{\circ} C$. The melting-point constituting the safest test for its identity and purity.

BORNEOL, $C_{10}H_{17}(OH)$, Borneo camphor, is found in all three modifications—dextro, levo and inactive. The common Borneo camphor is dextrogyrate, melting at 203° and obtained from the wood of *Dryobalanops camphora*.

MENTHOL, $C_{10}H_{19}(OH)$, mint camphor, is obtained from oil of peppermint (*Mentha piperita*) by chilling it. It is a secondary alcohol and yields *menthone*, a ketone on oxidation. Chemically, it is *hexahydroxycymene*:

DISCUSSION AND DESCRIPTION.—The essential or “volatile” oils have been so named after two facts: because they are “the essential odorous principles of plants” and because “they leave transient or volatile stains on paper,” this distinguishing them

from the fats. The essential oils differ from the fixed oils in the following points:

(1) In chemical composition: they are chiefly terpenes, and not esters of the fatty acids.

(2) They range in boiling-points from 150 to 250° C., volatilizing *without decomposition*.

(3) In their specific gravities they range from 0.83 to 1.187.

(4) They do not form soaps with the alkalis.

(5) They are slightly soluble in water and in definite proportions of alcohol. They are also freely soluble in the organic solvents. Many of the volatile oils, in addition to *C*, *H* and *O*, contain also *nitrogen*; some contain also *sulfur*. According to these constituents, oils are frequently classified for pharmaceutical purposes into:

(1) *Terpenes*, like the oils of lemon, orange, neroli, bergamot, etc.

(2) *Oxygenated*, like the oils of anise, cinnamon, clove, wintergreen, rose, etc.

(3) *Nitrogenated*, like the official oil of bitter almonds, peach kernels, etc.

(4) *Sulfurated*, like the volatile oil of mustard, garlic, asafetida, horseradish, etc.

They fulminate with iodine; react powerfully with nitric and sulfuric acids; are readily oxidized by the air, *acquiring color, resinifying*, etc., and *should be preserved in cool, dark place*, preferably in small completely filled bottles.

Adulteration.—Volatile oils are frequently adulterated with *alcohol*, which is *detected* by turning *milky*

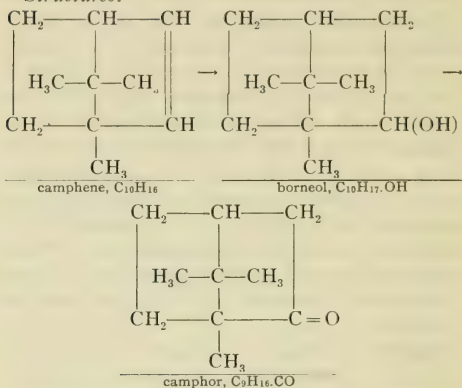
with water on agitation and by dissolving red anilin, which is insoluble in the oils. Fixed oils are detected by leaving a permanent stain on paper. Cheaper volatile oils can only be detected by the specific gravities, by the optical rotation and more frequently by the sense of smell. Many of the oxygenated oils are mixtures of liquid and solid principles; the former being solvents for the latter. These liquid principles are termed *eleoptenes*; the solid principles, *stearoptenes* or *camphors*. Thus, *menthol* is the *stearoptene* or *camphor* of peppermint oil. Thymol and camphor are both *stearoptenes*; these congeal upon chilling the oil and can be separated from the *eleoptenes*.

SAFROL, $C_{10}H_{10}O_2$ (safrolum U. S. P.), the methylene ether of pyrocatechol found in sassafras and camphor oils, is a *type of* the *eleoptenes*.

EUGENOL, $C_{10}H_{12}O$, U. S. P., is an unsaturated aromatic phenol found in clove and pimenta oils.

EUCALYPTOL, $C_{10}H_{18}O$ (cineol), is an inactive organic oxid, boiling at $176^{\circ} C.$; specific gravity, 0.93.

CAMPHORA MONOBROMATA, $C_{10}H_{15}BrO$, the monobromated camphor of pharmacy, is a substitution product of camphor and bromin. It is insoluble in water, soluble in other solvents, and used as a sedative.

Structures:

PREPARATION OF VOLATILE OILS.—Volatile oils are prepared after one of the *five methods* following:

(1) *By distillation with steam*; thus, the oils of peppermint, spearmint and rose are distilled from the coarsely comminuted drugs. The oils floating on top are separated. The condensed waters are sold as distilled “floral waters.” (2) *By expression*; where the oil is readily separated, as in the case of the oils of orange, lemon and bergamot peel.

(3) *By extraction with solvents*; in cases where the delicate oils would decompose with heat, they are extracted by macerating the flowers with odorless fixed oils or lard (*enfleurage*) from these they are dissolved out by alcohol which is distilled off in

vacuum. Oils of jasmin, tuberose, etc., are obtained thus.

(4) *By distillation of oleoresins*; thus, the oils of turpentine and copaiba are obtained.

(5) *By destructive distillation* are obtained the oils of tar and cade, from pine and juniper-wood, respectively.

THE IMPORTANT VOLATILE OILS.*

Name	Source	Method of extraction.	Sp. gr.	Constituents. (Those in italics are the percentages of constituents required by the U. S. P.)
Oleum amygdalæ amaræ (oil of bitter almonds)	seeds (<i>Amygdalus communis</i> var. amara)	maceration and distill.	1.043-1.049	<i>Benzaldehyd</i> , 85%; <i>hydrocyanic acid</i> , not less than 2, nor more than 4%.
Oleum anisi (oil of anise)	fruit (<i>Pimpinella anisum</i> or <i>Pimpinella</i>)	distillation	0.98	<i>Anethol</i> , $C_{10}H_{12}O$; anisic aldehyd, $C_8H_8O_2$; anisic acid; methyl chavicol $C_{10}H_{12}O$.
Oleum aurantii corticis (oil of orange peel)	fresh peel (<i>Citrus vulgaris</i> or <i>C. aurantium</i>)	mechanical means	0.860	Limonene, $C_{10}H_{16}$; citral, $C_{10}H_{16}O$; citronellal, $C_{10}H_{18}O$, and a crystalline ester.
Oil of orange flowers (neroli)	fresh flowers (<i>Citrus vulgaris</i>)	distillation	0.850-0.890	Limonene, $C_{10}H_{16}$; linalool, $C_{10}H_{18}O$; linalyl OH; geraniol, $C_{10}H_{18}O$; linalyl acetate, $C_{12}H_{20}O_2$; methyl anthranilate, $C_6H_5(NH_2)COO.CH_3$, and skatol.
Oil of bergamot	fresh peel (<i>Citrus bergamia</i> , var. vulgaris)	mechanical means	0.860-0.890	Linalyl acetate, $C_{12}H_{20}O_2$; bergapten, $C_{12}H_{14}O_4$. Limonene, $C_{10}H_{16}$; linalool, $C_{10}H_{18}O$.
Oleum betulæ (oil of sweet birch)	bark of <i>Betula lenta</i>	maceration and distill.	1.175	<i>Methyl salicylate</i> (99%), $C_8H_8O_2$; limonene, $C_{10}H_{16}$; triacontane, $C_{30}H_{62}$.
Oleum cadinum (oil of cade)	wood (<i>Juniperus oxycedrus</i>)	dry distill.		Cadinene, $C_{15}H_{24}$; phenols, $C_6H_4(OH)_2$, C_6H_5OH .
Oleum cajuputi (oil of cajuput)	leaves (<i>Melaleuca cajuputi</i>)	distillation	0.922	<i>Cineol</i> , 55% ($C_{10}H_{17}OH$); terpineol, $C_{10}H_{17}OH$; limonene, $C_{10}H_{16}$ and butyric and valeric aldehyds.
Oleum cari (oil of caraway)	fruit (<i>Carum carui</i>)	distillation	0.91	Carvone, $C_9H_{14}O$; limonene, $C_{10}H_{16}$.
Oleum caryophylli (oil of cloves)	flower buds (<i>Eugenia caryophyllata</i>)	distillation	1.06	<i>Eugenol</i> (80% vol.), $C_{10}H_{12}O_2$; caryophyllene, $C_{15}H_{24}$; clovene, $C_{15}H_{24}$; furool, $C_8H_{14}O_2$; amylmethyl ketone, $C_6H_{11}CO$.

* Oils whose *latin* titles are given in the tables are *official*, others are not.

THE IMPORTANT VOLATILE OILS.—Continued.

Name	Source	Method of extraction	Sp. gr.	Constituents. (Those in italics are the percentages of constituents required by the U. S. P.)
<i>Oleum chenopodii</i> (oil of American wormseed)	fruit (<i>Chenopodium anthelminticum</i>)	distillation	0.98	Terpene, $C_{10}H_{16}$; an alcohol, $C_{10}H_{17}OH$.
<i>Oleum cinnamomi</i> (oil of cinnamon)	bark of shoots (<i>Cinnamomum zeylanicum</i> and Chinese cinnamon)	distillation	Ceylon, 1.040 Chinese, 0.890	<i>Cinnamic aldehyd</i> , 75% vol. C_9H_8O ; eugenol, $C_{10}H_{12}O_2$; phellandrene, $C_{10}H_{16}$.
<i>Oleum copaibæ</i> (oil of copaiba)	oleo resin (<i>Copaiba</i>)	distillation	0.890	Caryophyllene, $C_{15}H_{24}$.
<i>Oleum coriandri</i> (oil of coriander)	fruit (<i>Coriandrum sativum</i>)	distillation	0.87	Linalool, $C_{10}H_{17}OH$; pinene, $C_{10}H_{16}$.
<i>Oleum cubebæ</i> (oil of cubeb)	unripe fruit (<i>Cubeba officinalis</i>)	distillation	0.921	Dipentene, $C_{10}H_{16}$; cadinene, $C_{15}H_{24}$; cubeb camphor, $C_{15}H_{26}O$.
<i>Oleum erigerontis</i> (oil of fleabane)	fresh fl. herb (<i>Erigeron canadensis</i>)	distillation	0.86	Terpineol, $C_{10}H_{17}OH$; limonene, $C_{10}H_{16}$.
<i>Oleum eucalypti</i> (oil of eucalyptus)	fresh leaves <i>Eucalyptus globulus</i> , etc.	distillation	0.92	<i>Cineol</i> , 50% (vol.), $C_{10}H_{17}OH$; pinene, $C_{10}H_{16}$; ethyl and amylalcohols; butyric, valeric and caproic aldehyds.
<i>Oleum foeniculi</i> (oil of fennel)	fruit (<i>Foeniculum vulgare</i>)	distillation	0.96	Pinene, limonene, dipentene, phellandrene—all $C_{10}H_{16}$; anethol $C_{10}H_{11}OH$; fenchone, $C_9H_{16}CO$.
<i>Oleum gaultheriæ</i> (oil of winter-green)	leaves (<i>Gaultheria procumbens</i>)	distillation	1.175	<i>Methyl salicylate</i> (99.8%), $C_8H_8O_3$; limonene, $C_{10}H_{16}$; triacontane, $C_{30}H_{62}$; a secondary alcohol, $C_7H_{14}CHOH$.
<i>Oleum hedeomæ</i> (oil of pennyroyal,	fresh herb (<i>Hedeoma pulegioides</i>)	distillation	0.93	Pulegone, $C_9H_{16}CO$; ketones of the formula $C_9H_{18}CO$; formic and acetic acids.
<i>Oleum juniperi</i> (oil of juniper berries)	fruit (<i>Juniperus communis</i>)	distillation	0.87	Cadinene, $C_{15}H_{24}$; pinene, $C_{10}H_{16}$; juniper camphor, melting-point, $165^{\circ}C$.

THE IMPORTANT VOLATILE OILS.—Continued.

Name	Source	Method of extraction	Sp. gr.	Constituents. (Those in italics are the percentages of constituents required by the U. S. P.)
Oil of lavender	fl. top or whole herb (<i>Lavendula vera</i>)	distillation	0.890	
<i>Oleum lavendulæ florum</i> (oil of lavender flowers)	fresh flowers (<i>Lavendula vera</i>)	distillation	0.88	Linalyl acetate, $C_{12}H_{20}O_2$ (about 8% in the English and 25 to 38% in the French oils); pinene and limonene, $C_{10}H_{16}$; geraniol and cineol, $C_{10}H_{17}OH$.
<i>Oleum limonis</i> (oil of lemon)	fresh peel (<i>Citrus limonum</i>)	mechanical means	0.850	<i>Citral</i> , 4%, $C_{10}H_{16}O$; limonene and phellandrene, $C_{10}H_{16}$; citronellal, $C_{10}H_{18}O$; linalyl and geranyl acetates, $C_{12}H_{20}O_2$.
<i>Oleum menthæ piperitæ</i> (oil of peppermint)	leaves of tops (<i>Mentha piperita</i>)	distillation	0.9	<i>Menthol</i> , 50% (wt.), $C_{10}H_{19}OH$; menthyl acetate, $C_{12}H_{22}O_2$; limonene, phellandrene, $C_{10}H_{16}$ acet-aldehyd and amylalcohol.
<i>Oleum menthæ viridis</i> (oil of spearmint)	leaves and tops (<i>Mentha viridis</i>)	distillation	0.93	Carvone, $C_9H_{14}CO$; limonene, pinene, $C_{10}H_{16}$.
Oil of bay	leaves (<i>Myrcia acris</i>)	distillation	1.040	Myrcene, $C_{10}H_{16}$; eugenol, $C_{10}H_{12}O_2$; methyl eugenol, $C_{11}H_{14}O_2$; phellandrene, $C_{10}H_{16}$; citral, $C_{10}H_{16}O$.
<i>Oleum myristicæ</i> (oil of nutmeg)	seed (<i>Myristica fragrans</i>)	distillation	0.9	Pinene, $C_{10}H_{16}$; myristicol, $C_{10}H_{18}OH$; myristician, $C_{12}H_{14}O_2$.
<i>Oleum picis liquidæ</i> (oil of tar)	oleo resin (<i>Pix liquida</i>)	distillation	0.970	Pinene, $C_{10}H_{16}$; cresols, $C_6H_4(OH)CH_3$.
<i>Oleum pimentæ</i> (oil of pimento)	fruit (<i>Eugenia pimenta</i>)	distillation	1.045	<i>Eugenol</i> , 65% (vol.), $C_{10}H_{12}O_2$; Caryophyllene, $C_{15}H_{24}$.
<i>Oleum rosæ</i> (oil of rose)	fresh fls. (<i>Rosa damascena</i>)	distillation	0.865	Geraniol, $C_{10}H_{16}OH$; citronellol, $C_{10}H_{17}OH$, and some aromatic hydrocarbons and alcohols.

THE IMPORTANT VOLATILE OILS.—Continued.

Name	Source	Method of extraction	Sp. gr.	Constituents. (Those in italics are the percentages of constituents required by the U. S. P.)
Oil of rue	herb (<i>Ruta graveolens</i>)	distillation	0.880	Methyl nonyl ketone, $C_{10}H_{22}CO$; lauric aldehyd.
Oleum rosmarini (oil of rosemary)	herb (<i>Rosmarinus officinalis</i>)	distillation	0.9	<i>Borneol</i> , 15%; and cineol, $C_{10}H_{17}OH$; camphene and pinene, $C_{10}H_{16}$; camphor, $C_9H_{16}CO$; bornyl acetate, $C_{12}H_{20}O_2$.
Oleum sabinae (oil of savin)	tops (<i>Juniperus sabina</i>)	distillation	0.92	Pinene, $C_{10}H_{16}$; cadinene, $C_{15}H_{24}$.
Oleum santali (oil of sandal wood)	wood (<i>Santalum album</i>)	distillation	0.97	<i>Santalol</i> , 90% (wt.), $C_{15}H_{26}O$; santalal, $C_{15}H_{24}O$; and isomeric santalol alcohols and esters.
Oleum sassafras (oil of sassafras)	bark of root (<i>Sassafras officinalis</i>)	distillation	1.07	Safrol, $C_{10}H_{10}O_2$; pinene and phellandrene, $C_{10}H_{16}$; cadinene, $C_{15}H_{24}$; camphor, $C_9H_{16}CO$; eugenol, $C_{10}H_{12}O_2$.
Oleum sinapis volatile (oil of mustard)	seed (<i>Sinapis nigra</i>)	maceration and distill.	1.017–1.021	<i>Allyl isothiocyanate</i> , 92%, $C_3H_3N = S = C$; carbon disulfid.
Oil of amber	fossil (amber) (succinum)	destructive distillation	0.920	Succinic, formic and acetic acids.
Oleum terebinthinæ (oil of turpentine)	oleo resin (<i>Pinus australis</i>)	distillation	0.855–0.870	Australene (d.pinenene), $C_{10}H_{16}$; dipentene, $C_{10}H_{16}$.
Oleum thymi (oil of thyme)	herb (<i>Thymus vulgaris</i>)	distillation	0.9	<i>Thymol</i> (<i>phenols</i>), 20%, $C_{10}H_{13}OH$; carvacrol, $C_{10}H_{13}OH$; borneol, $C_{10}H_{18}O$; cymene, $C_{10}H_{14}$; linalool, $C_{10}H_{17}OH$.
Oil of valerian	root (<i>Valeriana officinalis</i>)	distillation	0.950	Pinene, camphene, limonene, $C_{10}H_{16}$; borneol and terpineol $C_{10}H_{17}OH$; valeric aldehyd.

CHAPTER XXXIX.

THE PURIFICATION OF ORGANIC COMPOUNDS.

THERE are three methods used in the purification of organic compounds:

1. Crystallization
 2. Sublimation
 3. Distillation—in the case of liquids.
- } in the case of solids.

Solvents.—In the case where solids are to be purified by crystallization and recrystallization, determine *the best solvent*; one which dissolves the most of the salt while hot, and which, on cooling, crystallizes out the dissolved salt. Some *solvents* are inflammable; *others are not*. In cases where inflammable solvents are used, employ the steam-bath or water-bath to heat the same and *never the naked flame*.

Goggles should be used to protect the eyes while working with volatile solvents.

While *subliming* substances, the same should be mixed with about an equal quantity of pure sand which has been heated previously for about 10 minutes. The funnel used should have its mouth covered by a filter paper and the beak stopped up by means of a paper plug.

Some substances sublime without previous liquefaction, other liquefy first. (Try naphthaline, $C_{10}H_8$, and benzoic acid, C_6H_5COOH , as examples).

Distillations in vacuum and with *steam* are often

employed in the purification of liquids. The condensed vapor is frequently saturated with the dissolved substance and can be "salted out" by saturating the water with ordinary salt, and "taken up" with a volatile solvent like ether. The solutions of solids or liquids are frequently filtered through bone-black before crystallizing or separating them and are thus freed, from impurities.

BEHAVIOR OF ORGANIC SUBSTANCES WITH IMMISCIBLE SOLVENTS.

Upon agitating the substance with distilled water acidulated with 2% of H_2SO_4 , and adding half its volume of an immiscible solvent (ether, chloroform, or benzene), the following are extracted:

(1) *In the acidulated aqueous liquid there may be dissolved carbohydrates, soluble alkaloidal salts, acids, organic bases and proteins. Add a small excess of NaOH solution and half its volume of an immiscible solvent and again shake, thus further separating the above into (a) and (b).*

(a) The alkaline aqueous extract may contain:

Carbohydrates, as dextrin, sugars, gums.

Soluble alcohols, as methyl, ethyl, propenyl.

Soluble acids, as acetic, tartaric, citric, lactic, malic, oxalic.

Alkaloids and organic bases, as urea, curarine, cinchonine, pyridine and morphine.

Coloring matters, as indigo, cochineal, cudbear.

Proteids, as albumin, casein, gelatin.

(b) *The immiscible layer may contain:*

Vegetable alkaloids, as quinine, strychnine, aconitine, atropine, nicotine.

Coal-tar bases, as anilin, chrysotoluidin, pyridin and their homologues.

(2) *In the immiscible solvent* there may be dissolved hydrocarbons, oils, acids, coloring matters, resins, phenols and glucosids. Add water containing a small excess of NaOH and shake again, thus further separating the above into (a) and (b).

(a) *The alkaline aqueous extract may contain:*

Fatty acids, as stearic, oleic, palmitic, valeric.

Aromatic acids, as benzoic, salicylic, phthalic.

Acid coloring matters and dyes, as picric or chrysophanic acid, aurin, saffranin, alizarin or bilirubin.

Acid resins, as colophony (common pitches).

Phenols, as phenic and cresylic acids, thymol and creasote.

Glucosids, as santonin, picrotoxin.

(b) *The immiscible layer may contain:*

Hydrocarbons, solid, as paraffin, naphthalene, anthracene.

Hydrocarbons, liquid, as petroleum products, rosin-oil, benzene.

Essential oils, as turpentine, terpene and oxygenated oils.

Nitro-compounds, as nitrobenzene.

Chloroform, also ethers, as ethyl oxid, ethyl acetate, nitroglycerin, etc.

Fixed fats, oils and waxes.

Neutral resins and coloring matters.

Camphors, as laurel camphor, borneol, menthol.

Insoluble alcohols, as amyl, cetyl and cholesterin.

Glucosids, as saponin, santonin and digitalin.

Weak alkaloids, as caffeine, narcotine, piperine, colchicine.

THE ANALYSIS OF ORGANIC COMPOUNDS.

THE QUALITATIVE TESTS.

TESTS FOR CARBON.—(1) Any organic substance *chars*; if it chars, it is organic. A few inorganic compounds, like $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, also char, while some organic substances, as CHCl_3 , volatilize without first charring.

(2) Mix an organic substance with finely powdered CuO , heat and convey the gas into lime-water, CaCO_3 will be deposited in presence of organic compounds.

TEST FOR HYDROGEN.—Heat the dry substance in a dry test-tube; if moisture or drops of H_2O collect in the upper portion of the tube, *hydrogen* is present. *Or, heat the substance with CuO , when water will form.*

Quantitatively, H_2 may be estimated by passing the gas formed through CaCl_2 tube previously weighed. H_2 being $\frac{1}{9}$ of the H_2O found.

TEST FOR NITROGEN.—(1) When organic substance is heated with soda lime, which is a mixture of equal parts of CaO and NaOH (heated together until perfectly dry), ammonia (NH_3) is formed. Heat, hold a piece of turmeric paper over the mouth of the

tube, and a brown spot will form. *This test is not universal.*

RELIABLE TEST FOR NITROGEN.—(2) A piece of metallic sodium (half a pea size) is placed in a long, narrow test-tube with some of the substance to be tested. Heat slowly, and carefully, until redness is reached.

Protect the eyes.

The C and the N will unite with the Na to form Na(CN). Break the tube in water, heat the water to extract the cyanid, filter from carbonaceous matter, and add FeSO_4 to the solution, then HCl to acidify, and heat. The alkaline $\text{Na(CN)} + \text{FeSO}_4 = \text{Fe(OH)}_2$ which is precipitated, and sodium ferrocyanid formed; thus:

$$6\text{Na(CN)} + \text{Fe(OH)}_2 = \text{Na}_4\text{Fe(CN)}_6 + 2\text{NaOH}$$
and on addition of $\text{FeCl}_3 =$ ferric ferrocyanid or Prussian blue is formed. (Use dry acetamid or quinolin for this test.)

TEST FOR HALOGENS.—(1) *The simplest* test is to heat a copper wire until it ceases to color the flame green. A small quantity of an organic halogen compound is now heated on the end of the wire in the flame, which in the presence of halogen compounds will produce or acquire a green coloration. (Use CHI_3 for a solid halid and CHCl_3 for a liquid). This test *sometimes fails*.

(2) *Test for halogens in the presence of S or N.*—Acidify the solution with dilute H_2SO_4 , boil for 5 minutes in open vessel to expel the H_2S formed and the HCN. Filter, acidify with dilute HNO_3 ; to 1 c.c.

of the solution add a few drops AgNO_3 solution. If a precipitate forms, acidify a larger portion with HCl , add a few drops of CS_2 and then Cl_2 water drop by drop, continuing the addition if I is present, until the violet color disappears.

(3) *Tests for Halogens in Absence of N or S.*—This is the same as above; omit the treatment with H_2SO_4 and the boiling for 5 minutes.

TESTS FOR PHOSPHORUS AND SULFUR IN ORGANIC COMPOUNDS.—Sulfur and phosphorus may be detected and estimated by heating the substance with nitric acid. This is done in a sealed tube provided with a capillary tube; and it should be remembered that great care is necessary in breaking the capillary tube open. By the heating, the sulfur will be oxidized entirely to H_2SO_4 and the phosphorus to H_3PO_4 . These can be tested for by appropriate reagents qualitatively or estimated quantitatively by the usual methods.

ELEMENTARY ORGANIC ANALYSIS.

In the discussion under this head we will present, in outline only, principles of chemical analysis, by means of which we may determine the percentage composition and the *empiric formulas* of compounds containing *carbon, hydrogen, oxygen and nitrogen*, and also *sulfur and phosphorus*.

CARBON AND HYDROGEN.—These elements are determined by burning the body, at a red heat, in a "combustion tube" of glass, porcelain or platinum, with oxygen. Under such circumstances, the carbon

of the compound is burned to carbon dioxide, CO_2 ; and the hydrogen is burned to steam, H_2O . The gaseous products, CO_2 and H_2O , are aspirated through a weighed tube containing dry calcium chloride, CaCl_2 . The H_2O is absorbed by the CaCl_2 and the increase in weight of the tube is the weight of water absorbed. The CO_2 is further aspirated through a weighed tube filled with grains of a mechanical mixture of sodium hydroxide (NaOH) with lime (CaO). The CO_2 is absorbed in this tube, forming sodium carbonate, Na_2CO_3 ; and the increase in weight of the "soda lime" tube, is the weight of CO_2 absorbed. Having determined its weight, we are now in a position to calculate the percentages of carbon and hydrogen in the body under examination. We must first calculate the weights of carbon and hydrogen from the observed weights of CO_2 and H_2O ; thus:

$$\text{CO}_2 : \text{C} = 44 : 12.$$

$44 : 12 = \text{observed weight of } \text{CO}_2 : \text{required weight of C.}$

$$\text{H}_2\text{O} : \text{H}_2 = 18 : 2.$$

$18 : 2 = \text{observed weight of } \text{H}_2\text{O} : \text{required weight of } \text{H}_2.$

Now calculate percentages, thus:

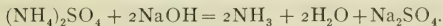
$$\frac{\text{Weight of carbon determined}}{\text{Weight of body taken}} \times 100 = \text{per cent. of carbon in the body.}$$

$$\frac{\text{Weight of hydrogen determined}}{\text{Weight of body taken}} \times 100 = \text{per cent. of hydrogen in the body.}$$

NITROGEN.—This element is most conveniently determined by the method of *Kjeldahl*. The principles concerned are as follows:

I. The nitrogenous body is vigorously boiled in concentrated sulfuric acid (H_2SO_4). This treatment so operates as to bring about the formation of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, which salt contains all of the original nitrogen of the body under examination.

II. Solution I is made strongly alkalin with sodium hydroxid (NaOH) and then boiled. The ammonium sulfate is decomposed by this process with the formation of sodium sulfate, Na_2SO_4 , and the liberation of ammonia gas (NH_3):



III. The NH_3 liberated from solution II is conducted into, and absorbed by, a solution that contains a known weight of hydrochloric acid, HCl , the HCl being in excess: $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$.

A portion of the HCl is thus neutralized by the NH_3 .

IV. Solution III is *titred* with a *standard* solution of NaOH , using phenol-phthalein or another efficient indicator. The excess of HCl is thus determined, from which the quantity of HCl required to neutralize the NH_3 is obtained by subtraction.

V. Calculate the HCl equivalent to nitrogen (in ammonia), thus:

$$\text{HCl} : \text{N} = 36.5 : 14.$$

$36.5 : 14 =$ weight of HCl used to neutralize the NH_3 : required weight of nitrogen.

VI. Calculate the percentage of nitrogen; thus:

$$\frac{\text{Weight of nitrogen determined}}{\text{Weight of body taken}} \times 100 = \text{per cent. of nitrogen in the body.}$$

VOLUMETRIC ANALYSIS.—We have used the terms *titre* and *standard solution* in explaining *Kjeldahl's* method for the determination of nitrogen in organic bodies. It is necessary that the meaning of these terms should be explained.

The principle upon which volumetric analyses are based is this: By means of the balance we prepare a solution, one unit volume of which (usually 1 c.c.) is made to contain a certain weight of some chemically active substance—the exact substance used being dependent upon the particular analysis we desire to make. Such a *known* solution, is called a *standard* or *volumetric* solution.

A standard or volumetric solution of any chemically active substance is called a *normal* $\left[\frac{N}{I} \right]$ solution when it contains in one liter (1000 c.c.) as much of the chemically active substance as is equivalent to one gram of hydrogen.

If, now, in the course of an analysis, we prepare another solution that contains an unknown weight of some body that can enter into a definite chemical reaction with the body in the standard solution, the standard solution furnishes us with means for determining the actual weight of active material in the unknown solution. It is only necessary for us to measure the number of unit volumes of the standard

solution required to conclude a certain reaction with all of the active material in the unknown solution. Then, since each unit volume of the standard solution corresponds or is equivalent to a definite weight of the active body in the unknown solution, it is simply necessary to multiply the number of unit volumes of standard solution used by the previously determined factor which expresses the weight of active material in the unknown solution equivalent to one unit volume of the known or standard solution.

We are, therefore, required to have some means both for measuring the volume of standard solution used and for determining when the reaction has been fully completed. In order to measure the volume of standard solution employed, we make use of a narrow, graduated glass cylinder, called a *burette*. In order to tell the end point of our *titration*, we make use of a solution of some body that is capable of causing a **marked** color change with a minute quantity of our standard solution, but cannot do so as long as any of the active material in the unknown solution remains unacted upon. Such a body is termed an *indicator*, because it indicates the completion of the principal reaction.

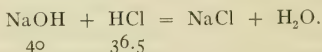
Passing from the above general exposition of the nature of volumetric analyses and coming to the Kjeldahl method for the determination of nitrogen, we have to consider the quantitative relations of the reaction between NH_3 and HCl . The reaction is written:



Therefore, 14 parts of nitrogen correspond to 36.5 parts of hydrochloric acid.

In the course of our analyses we obtained a solution that contained all of our nitrogen as ammonia. This would be our unknown solution—for, while we know that it contains all of our nitrogen as ammonia, we do not know the weight present.

Let us now have prepared two standard solutions—one containing 3.65 grams of HCl per litre (= .00365 grams per c.c.); and the other containing 4 grams of NaOH per liter (= .004 grams per c.c.) Any given volume of either of these solutions would be exactly equivalent to the same volume of the other, thus:



Suppose that the body being analyzed weighed 5 grams and that its nitrogen after being changed to ammonia was distilled into 50 c.c. of our standard HCl. Some of the HCl would have been changed to neutral NH_4Cl . Now add a few drops of an alcoholic solution of phenolphthalein (which is colorless in the presence of free HCl, but is crimson in the presence of free NaOH); and then run into the solution from a burette NaOH solution until a red color appears. Suppose that 30 c.c. NaOH solution accomplished this result. Evidently $50 - 30 = 20$ c.c. of our HCl was neutralized by the unknown weight of NH_3 . But as 1 c.c. HCl we know to be equivalent to .0014 gram of nitrogen. Therefore, if our 5 grams of sample contained $.0014 \times 20 = .028$ gram

of nitrogen. The percentage of nitrogen is therefore

$$\frac{0.028}{5} \times 100 = .56\%.$$

Note.—By means of special volumetric analyses we determine, clinically, the quantitative composition of urines, gastric juice, water, and drug strength, etc.

DETERMINATION OF SULFUR AND PHOSPHORUS.

In order to determine the percentage of sulfur and phosphorus in organic bodies, we heat the bodies with strong nitric acid. By this treatment the sulphur is converted to sulfuric acid and the phosphorus to orthophosphoric acid. These are precipitated separately (the sulfuric acid by barium chlorid in the presence of hydrochloric acid; and the phosphoric acid by magnesium chlorid in the presence of ammonium hydroxid) and weighed, after ignition in a platinum crucible, as barium sulfate (BaSO_4), and magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), respectively. The weight of BaSO_4 and $\text{Mg}_2\text{P}_2\text{O}_7$ are calculated to S and P_2 , respectively; and thence the percentage of sulfur and phosphorus in the organic body obtained.

Determination of Oxygen.—Oxygen, being difficult to determine directly, is usually determined by difference. We determine all the other elements in the body, and subtract the sum of the percentages from 100. The remainder is taken as being the percentage of oxygen.

Calculating Empiric Formulas.

Having obtained the percentages of the various

elements that enter into the composition of the organic body under examination, we are in a position to calculate its empiric formula.

By the empiric formula for a body we mean the simplest formula that shows a composition in harmony with our elementary analysis.

The method for calculating empirical formulas will be understood from an inspection of the subjoined example. An elementary analysis of lactic acid showed that it has the following elementary composition:

Carbon	=	40.00 per cent.
Hydrogen	=	6.6 per cent.
Oxygen	=	<u>53.4</u> per cent.
in		100.00 parts.

Divide the above numbers by the respective atomic weights:

$$\frac{40}{12} = 3.3 \quad \frac{6.6}{1} = 6.6 \quad \frac{53.4}{16} = 3.3$$

C., H., O.

$$\begin{array}{l} \text{The ratio, therefore, is} \\ \text{or} \end{array} \quad \begin{array}{l} = 3.3 : 6.6 : 3.3 = \\ = 1 : 2 : 1 \end{array}$$

The carbon and oxygen atoms are, therefore, equally numerous in lactic acid, but the hydrogen atoms are twice as numerous as either the carbon atoms or the oxygen atoms. The simplest formula for lactic acid is, therefore, CH_2O .

UNSATISFACTORY NATURE OF EMPIRIC FORMULAS.

We have seen above that the formula CH_2O expresses an elementary composition in entire accord-

ance with our analytical knowledge concerning lactic acid. But that this formula is quite irrational is evidenced by the fact that we know *a number of bodies* that have properties widely *differing from* the properties of *lactic acid*; but to which we would give an *identical empiric formula*. Such bodies are formaldehyd, formose, grape-sugar, fruit-sugar, acetic acid, etc.

A *rational formula* for lactic acid would show the manner in which lactic acid differs from the other bodies mentioned. Now the formula for lactic acid may very well be some *multiple* of CH_2O . We must, therefore, write $(\text{CH}_2\text{O})_n$ as the formula for lactic acid. The "n" meaning some definite whole number as yet undetermined. We are, therefore, at this stage entirely unacquainted with the true molecular weight of lactic acid, and have no means for explaining why its properties should be expected to differ from those of certain other bodies having an identical percentage composition.

DETERMINATION OF TRUE MOLECULAR WEIGHT.

We have a number of methods by means of which we may arrive at conclusions as to the molecular weights of bodies. Two of these methods we will now discuss.

Molecular Weight by Chemical Reasonings.—Let us consider the well-known compound, water, seeking to discover how many times heavier is its molecule than an atom of hydrogen.

From our analyses of water, we know it to be composed of hydrogen, one part, and oxygen, eight parts, by weight. Each molecule of water, therefore, contains at least one atom of hydrogen and one atom of oxygen. We might for the moment write the formula HO (which would make oxygen have an atomic weight of 8).

Now, 23 parts of the element sodium can react with 18 parts of water, liberating 1 part of hydrogen; and forming a perfectly definite compound that contains all of the sodium that was used, all of the oxygen from the water, and one-half of the hydrogen from the water. It is a primary conception that an atom cannot be divided; and, since we have observed that the hydrogen in the water molecule can be split into two equal parts, it is an unavoidable conclusion that the molecule of water must contain *at least* two atoms of hydrogen. We are consequently in a position to write the formula H_2O for the molecule of water.

No experiment has ever shown that the hydrogen in the water molecule can be divided into more than two parts. Also, no one has ever been able to divide the oxygen in the water molecule. We have, then, most excellent reasons for writing the formula H_2O as truly expressing the molecule of water. But the atom of hydrogen is taken as unity; the hydrogen in the water molecule, therefore, weighs two, and, since we know by analysis that water has eight times as much oxygen as hydrogen, it follows that the oxygen in the water molecule must weigh ($2 \times 8 = 16$) sixteen. The molecular weight of water is, therefore

($2 + 16 = 18$), eighteen; or, in other words, the molecule of water weighs eighteen times as much as one atom of hydrogen.

By similar reasonings we could come to the conclusion that the molecule of hydrochloric acid contains one atom of hydrogen. We know by analysis that one part by weight of hydrogen in hydrochloric acid can be displaced by 107.7 parts by weight of silver, with the production of silver chlorid. Therefore, 107.7 parts by weight of silver (which has been set as the atomic weight of silver) is equivalent to one acid hydrogen atom.

It is quite easy for us to prepare silver lactate and to analyze the salt. We find that the same weight of silver (107.7) as is equivalent to one molecule of hydrochloric acid (36.5) is also equivalent to 90 parts of lactic acid. Lactic acid, therefore, contains one acid hydrogen atom and has a molecular weight of 90.

The formula CH_2O , however, gives us a molecular weight ($12 + 2 + 16 = 30$) of 30. We must, therefore ($30 \times 3 = 90$), triple our formula CH_2O , and write the formula for lactic acid $(\text{CH}_2\text{O})_3$. We have thus found our previously unknown "n" to be 3.

We know, nevertheless, that the body trioxymethylene has the formula $(\text{CH}_2\text{O})_3$ (*i.e.*, it is identical with lactic acid in elementary composition and molecular weight); and we are, consequently, still without means for saying why we should expect the two bodies to be so very different in their properties as we know them to be. When we come to study the structures of the

respective molecules, we will be furnished with our desired explanation.

We will now consider another example: Ethane is a well-known gas. Analysis shows it to have the following composition:

Carbon = 4 parts (80%).

Hydrogen = 1 part (20%).

Calculate the empiric formula:

$$\frac{4}{12} = \frac{1}{3} \qquad \frac{1}{1} = 1.$$

The hydrogen atoms are thus three times as numerous as the carbon atoms in the molecule of ethane. We thus arrive at the empiric formula: $(\text{CH}_3)_n$.

But we find that $\frac{1}{6}$ of the hydrogen in the ethane molecule may be replaced by chlorine, with the production of the definite body, ethyl chlorid. The ethane molecule must, therefore, contain at least six hydrogen atoms and the formula must be C_2H_6 ; i.e., "n" here is equal to two.

Molecular Weight by Avogadro's Law.—The famous law of the Italian physicist, Avogadro, may be stated thus: "Equal volumes of all gases, at the same temperature and pressure, contain equal numbers of molecules." It, obviously, follows at once, from this law, that the relative weights of the molecules of the various gases are proportional to the relative densities of the gases.

It is, therefore, in fixing molecular weights by the application of Avogadro's law, first necessary to fix

the molecular weight of hydrogen (the hydrogen atom being the unit of mass); and then to determine the densities of other gases relative to the density of hydrogen. The hydrogen molecule is known to contain at least two atoms of hydrogen; and is not known to contain more than two atoms. The molecule of hydrogen, therefore, weighs two. The density of hydrogen is taken as one. The molecular weight of hydrogen being, thus, twice its density, it follows that the molecular weight of any gas is twice its density (compared with hydrogen).

So, in order to set the molecular weight of any body by the law of Avogadro, we determine how many times heavier is any volume of the body *in the gaseous state* than the same volume of hydrogen. The density figure being determined, it is multiplied by two; and the product is the molecular weight of the body (in its gaseous state).

This method for determining molecular weights is far simpler and much more direct than the chemical method; but it is only applicable to gases and to such liquids and solids as can be vaporized without decomposition.

The molecular weight of a body as set by purely chemical methods is always identical with the molecular weight determined by the application of Avogadro's law.

Examples:

Gas	Density (Hydrogen = 1)	Molecular weight Density \times 2
Steam	9.	18.
Hydrochloric acid..	18.25	36.5
Ethane	15.	30.
Ethyl chlorid	32.25	64.5
etc.	etc.	etc.

The two methods of vapor density determination prominently mentioned are:

(a) **THE CRYOSCOPIC METHOD.**—Depending upon the depression produced in the freezing-point of a solvent by a known weight of the substance. This was the original method and known as the “freezing-point method” or “Beckmann method.”

(b) **THE VICTOR MEYER METHOD.**—Dependent, as stated before, on the comparison of the *vapor* density with a *standard* (hydrogen). The substance is converted into a *vapor*, which *displaces air*. This vapor is caught in a graduated tube of the apparatus. The collected *volume* of gas is *corrected for temperature and pressure* to 0° and 760 mm. of mercury. The weight of this corrected volume is compared with the weight of the same volume of hydrogen (standard). To illustrate: 0.073 gm. of ether displaced 25.3 c.c. of air. The column of displaced air was read at 21.5° and 718.6 mm. pressure. What was the volume of the ether vapor?

$$25.3 \times \frac{273^{\circ}}{273^{\circ} + 21.5^{\circ}} = 23.46 \text{ c.c. of vapor.}$$

This corrected for pressure:

718.6 less 19.1 (vapor tension of H_2O at 21.5°)
= 699.5 mm.

Then—

$23.46 \text{ c.c.} \times \frac{699.5}{760} = 21.5 \text{ c.c. of ether vapor —}$
at 0° C. and 760 mm. pressure.

This volume of hydrogen weighs, $\frac{21.5 \times .09}{1.000} =$
0.00197 gram of H_2 .

The quantity of ether originally taken divided by
the equivalent weight of hydrogen, $\frac{.073}{.00197} = 37.6$
specific gravity of the ether vapor.

TOXICOLOGY.

Toxicology is a branch of medical science which treats of poisons. In this short article are included the definitions, effects on the living body, symptoms and treatment within the body. Also an abstract of the Pennsylvania poison law.

True poison may be defined as a substance which when absorbed by the system produces great physical injury or death. Examples: hydrocyanic acid, morphine, strychnine.

A corrosive poison is a substance which destroys the tissues with which it comes in contact. Examples: the acids, like sulfuric and nitric.

These two main classes of poisons should be distinguished; thus: Sulfuric acid, which is a *corrosive*, burns the tissues with which it comes in contact; strychnine, which is a *true poison*, on the other

hand, will do *no injury to the tissues*, but when **absorbed** into the blood it will produce death.

Sulfuric acid, *largely diluted*, loses its *corrosive properties*; strychnine is *no less poisonous whatever the dilution*.

Some poisons, like *corrosive sublimate* and *arsenic*, possess the properties of both true and corrosive poisons, and are called *irritant poisons*. The State Pharmaceutical Examining Board in their instructions to the pharmacists regard as *a poison, any drug, chemical or preparation* which, according to standard works on medicine or materia medica, is liable to be *destructive to adult human life in quantities of sixty grains or less*.

Substances which produce deleterious effects or cause death due solely to mechanic action are not poisons. The taking into the system of such substances as crushed glass, metal filings, boiling water, etc., may produce injury or death due solely to mechanic action.

A *cumulative poison* is one that slowly collects in the system when taken *for some time*. Such are digitalis, mercury, lead, iodine, etc.

Poisons may be administered with some other criminal intent than that of murder; the criminal administration of abortifacients and the use of narcotics in attempted robberies, etc., being well-known examples.

The effects of poisons are both local and remote. The former being the direct impression on the tissue with which the poison may come in contact (e.g., the corrosive effect of the mineral acids on the skin or

mucous membrane). *The latter* are those *resulting from the action of the poison upon the blood, brain or spinal cord* after having gained entrance into the system (e.g., the tetanic effect of a large dose of strychnine on the spinal cord after being absorbed from the stomach). Some poisons act both locally and remotely (e.g., arsenic acts locally on the stomach and remotely on the brain). The usual symptoms of poisoning are due to the remote effects and are of value in the diagnosis of a case.

Various conditions which affect the toxic action of poisons: (1) Dose; (2) age; (3) habit; (4) idiosyncrasy; (5) state of health; (6) the condition in which the poison is administered; (7) the mode of introduction into the system; (8) the amount of food in the stomach at the time the poison is administered or taken; (9) combination of poisons.

Poisoning may be *acute*, when produced by taking one large dose of poison; *chronic*, when produced by long continued absorption of minute quantities of the poison; thus: *mercurialism*, produced by long-continued dosing with mercury salts; *saturnism*, produced in painters and plumbers working with *lead* (lead-poisoning); *iodism*, *cinchonism*, etc., are all forms of *chronic poisoning*.

AN ANTIDOTE is any measure or agent, which counteracts the effects of a poison or an attack of disease. Antidotes are *divided* into *mechanic*, *chemic* and *physiologic*.

Examples of **MECHANIC ANTIDOTES** may be had in the stomach-pump, demulcents, as flour paste,

mucilages, fixed oils and egg albumen. This last agent serves also as a chemical antidote for copper and mercury, forming albuminates (excess should be avoided in mercury poisoning as it forms a soluble *double albuminate*).

CHEMIC ANTIDOTE is one which combines with the poison, forming *harmless* or *insoluble* compounds; thus, magnesium oxid with the corrosive acids forms *harmless sulfate, chlorid* or *nitrate*, etc.; common salt precipitates *lunar caustic* and *other silver salts* forming insoluble silver chlorid.

A **PHYSIOLOGIC ANTIDOTE**, also called "antagonist," is one which produces opposite—antagonistic—effects in the system; thus, *physostigma* is *antagonistic* to *strychnine*; *digitalis* antagonizes *aconite*; *atropine* antagonizes *morphine*. The physiologic antagonists are *best administered hypodermically*.

CONTRAINDICATION OF ANTIDOTES.—The *stomach-pump* should never be used in strong mineral acid or oxalic acid, strong alkali or corrosive sublimate poisoning (perforation of esophagus or stomach may result). *Alkalis*, should never be used in neutralizing oxalic acid (the alkaline oxalates are poisonous and more soluble); the alkali carbonates are contraindicated in corrosive acid poisoning (CO_2 is given off, which is apt to rupture the corroded stomach and intestines). *Oils* should never be used in phosphorus, phenol, creasote and cantharides poisoning (they dissolve phosphorus and cantharidin, etc.).

TREATMENT OF UNKNOWN POISONING.—In

the case where the poison is unknown, administer *Jeannel's universal antidote*, composed of solution ferric sulfate, 75 c.c.; magnesium oxid, 60 gm.; animal charcoal, 30 gm.; water, 600 c.c.; give in 2 wineglassful doses every 3 minutes. This is also known as the "*multiple antidote*," and acts as follows: The magnesia neutralizes any acid present, the iron salt combines with any arsenical poison, and the charcoal absorbs or precipitates any alkaloid. This treatment should, if necessary, be followed with stimulants until the physician arrives.

The **STIMULANTS** generally used in poisoning cases are: brandy, whisky, alcohol, ether, tincture of capsicum per rectum, strong tea or coffee. Strong coffee, preceded by emetic and a little tannin, is a reliable antidote for the narcotic (solanaceæ) poisons.

SPECIAL SYMPTOMS SUGGESTING CERTAIN COMMON POISONS.

Organic.

- (1) *Aconite*: numbness, tingling and paralysis.
- (2) *Alcohol* (acute): unconsciousness, dilated pupils, cold skin.
- (3) *Belladonna, atropine*: active delirium, dilated pupils, hot skin, etc. (this applies to all the solanaceæ).
- (4) *Conium*: paralysis of limbs; vertigo, convulsions, mind clear, double vision.
- (5) *Digitalis*: heart very slow, rapid during movement, with nausea, pain, vertigo, disturbed vision.
- (6) *Headache powders* (phenacetin, antipyrin,

acetanilid): depression, vomiting, blueness of lips chilliness, collapse.

(7) *Nux vomica*: severe convulsions and spasms, opisthotonos, clear intellect until the end.

(8) *Opium and its preparations*: unconsciousness, contracted pupils, congestion.

(9) *Phenol* (carbolic acid): note odor or stains.

(10) *Ptomain or mushroom poisoning*: severe vomiting and purging, chills, collapse.

(11) *Santonin*: yellow color of urine; yellow vision.

Inorganic.

(1) *Acids and corrosive irritants*: great pain, cold skin, collapse.

(2) *Antimony and copper*: same as above; but in the latter the vomited matter is green or blue.

(3) *Arsenic*: severe vomiting, severe burning in the mouth, esophagus (gullet) and stomach, bloody stools, convulsions, cold sweats, coma (unconsciousness).

(4) *Alkalis*: severe burning in throat and stomach, stricture of esophagus, violent pains in stomach, cold skin, etc.

(5) *Corrosive sublimate*: practically the same symptoms as arsenic, but appearing more rapidly.

(6) *Hydrocyanic acid and cyanids*: death rapid, symptoms rarely noted. Short convulsions, odor of almond oil may be noticeable.

(7) *Iodin, bromin*: similar symptoms to last, but not quite so severe.

(8) *Lead salts*: burning pains in throat and stom-

ach, thirst, intense colicky pains in abdomen. In chronic poisoning: severe colic (lead colic), paralysis of hands and feet (lead palsy); blueness of gums, obstinate constipation.

(9) *Mineral acids*: severe burning in throat and stomach, severe vomiting of black or reddish matter, convulsions, pains in bowels.

(10) *Phosphorus*: Abdominal pains, severe vomiting (having odor of garlic), jaundice, suppressed urine, delirium (vomited matter phosphorescent in the dark).

(11) *Silver nitrate* (treatment same as antimony and copper): hard white patches about mouth (turning black in time).

GENERAL METHOD OF TREATMENT OF CASES OF POISONING.

In the treatment of cases of poisoning the following general method is recommended:

(1) Remove the poison from the stomach or chemically and mechanically antidote the poison.

(2) Administer physiologic antidotes or adopt such measures as will antagonize the action of that portion of the poison which has been absorbed.

(3) Promote the elimination of that portion of the poison which has been absorbed from the system by resorting to such means as the nature of the poison may suggest.

(4) Combat any dangerous symptoms and endeavor to keep the patient alive until the toxic effects have disappeared.

These general methods require brief discussion:

(1) Removal of the poison from the stomach may be accomplished by the induction of vomiting by the use of emetics or by tickling the fauces or by the use of the stomach-pump or stomach-tube.

Emetics are classified, according to their physiologic action, into two kinds:

Peripheral and Centric.—*Peripheral emetics act locally*, principally upon the terminations of vagi in the stomach or locally upon the terminations of the fifth and glossopharyngeal nerves in the mucous membrane of the fauces. *Centric emetics act by stimulating the vomiting center in the medulla oblongata.* Some examples of emetics:

Flour of mustard, $\frac{1}{2}$ to 2 tablespoonfuls in $\frac{1}{2}$ glass of water.

Tartar emetic, $\frac{1}{2}$ to 1 grain (wine of antimony contains two grains of tartar emetic to each ounce).

Zinc sulfate, 15 to 30 grains.

Powdered ipecac, 15 to 30 grains.

Ammonium carbonate, 15 to 30 grains.

Copper sulfate, 5 to 10 grains.

Apomorphine, $\frac{1}{10}$ grain hypodermically.

Copious draughts of tepid water.

Mustard irritates the gastric mucous membrane and is a good example of a peripheral emetic. Apomorphine stimulates the vomiting center and is a typical centric emetic. Antimony (tartar emetic) acts in both ways: it irritates the gastric mucous membrane and also stimulates the vomiting center in the medulla.

Poisons may be removed from the stomach by means of the stomach-pump or the stomach-tube, and the stomach in the use of either may at the same time be washed out.

POISONS AND THEIR ANTIDOTES.

Poison	Antidotes
(1) <i>Mineral Acids.</i> (H_2SO_4 HNO_3 HCl and nitro - hydro- chloric acid.)	Give no emetic. Magnesia mixed with water, milk, whitening, fixed oils, demulcents, Laudanum (20 drops) if much pain. (<i>No stomach-pump.</i>)
(2) <i>Vegetable Acids.</i> (Oxalic acids and salts; tartaric acids and salts.)	Chalk, whiting, air-slacked lime with vinegar. (No soda or potash to neutralize acid.) Mustard water, olive oil, demulcents and stimulants. (<i>No stomach-pump.</i>)
(3) <i>Alkalis.</i> (NaOH , KOH , $\text{NH}_4\text{-OH}$ and their carbonates.)	Warm water till emetic; vinegar, lemon juice or citric acid. Olive oil, demulcents, and Tr. opium (20 drops) if much pain. (<i>No stomach-pump.</i>)
(4) <i>Barium, lead and their salts.</i>	Epsom ($\frac{1}{2}$ oz.) or Glauber's salt (1 oz.) in water. Emetic (mustard water), milk and demulcents, and laudanum if needed.
(5) <i>Arsenic and all its compounds.</i>	Emetic (mustard water), hydroxid of iron or hydroxid of iron with magnesia, olive oil, albumen, demulcents and Tr. opium.
(6) <i>Antimony salts, cantharides, colchicum, eluterium, iodin, copper, mercury, croton oil, savin, tansy, potass. bichromate, tin and zinc salts.</i>	Albumen diffused in water. Emetics (warm) water with NaHCO_3 or mustard), strong tea or coffee, or tannin, stimulants, Tr. opium (if needed) and demulcents.

POISONS AND THEIR ANTIDOTES.—*Continued.*

Poison	Antidotes
(7) <i>Nux vomica</i> and <i>strychnine</i> .	Emetics (mustard water), powdered charcoal, iodized starch or tannin. To relieve spasms inhalations of chloroform or, internally, 25 grs. chloral hydrate or $\frac{1}{2}$ oz. potassium bromid. Lose no time.
(8) <i>Silver nitrate</i> .	Sodium chlorid, emetics (mustard water), demulcents.
(9) <i>Cannabis indica</i> , <i>opium</i> and <i>morphine</i> .	Emetics (mustard water) or stomach-pump, cold affusions, strong tea or coffee; electro-magnetism. Keep patient awake and in motion. Artificial respiration.
(10) <i>Aconite</i> , <i>digitalis</i> , <i>ergot</i> , <i>lobelia</i> , <i>tobacco</i> , <i>veratrum</i> , <i>belladonna</i> , <i>coniium</i> , <i>henbane</i> , <i>santonin</i> , <i>stramonium</i> , <i>calabar bean</i> .	Emetics (mustard water), strong tea or coffee. Hypodermics of morphine; powdered charcoal; stimulants, (whisky), etc. Warmth to extremities and artificial respirations.
(11) <i>Phosphorus</i> .	Emetics (CuSO_4 , 3 grains every 5 min.) $\text{f}\overline{3}\text{i}$ old oil turpentine, MgSO_4 ($\frac{1}{2}$ oz.). No oils.
(12) <i>Alcohol</i> , <i>chloral</i> , <i>ether</i> , <i>chloroform</i> .	Emetics (mustard mixture), stomach-pump, strong coffee or tea, cold affusions, artificial respiration, mustard poultice to limbs.
(13) <i>Hydrocyanic acid</i> and <i>the cyanids</i> .	Mild inhalations of ammonia, cold applications to head; internally, the following three solutions in order given: (a) Potassium carbonate, 15 grains, in H_2O , $\text{rf}\overline{3}$; (b) iron sulfate, 15 grains in H_2O , $\text{rf}\overline{3}$; (c) tincture iron chlorid, $\text{rf}\overline{3}$. (This forms the harmless "Prussian blue.")

ABSTRACT OF THE PENNSYLVANIA POISON LAW.

Unregistered dealers may sell the commonly used drugs and medicines in packages that have been legally prepared by or under the supervision of registered pharmacists.

After the law in regard to the mixing or compounding and dispensing of drugs, medicines and medicinal preparations has been complied with, it is permissible for general storekeepers and merchants who are not registered pharmacists *to sell* legally prepared packages of the commonly used medicines and poisons, subject, of course, to the same restrictions that are placed upon properly qualified and registered pharmacists in regard to purity and strength under the Act of May 25, 1897; and under the restrictions of Section 10 of the Act of 1887, which is as follows:

“SECTION 10.—*A poison*, in the meaning of this Act, shall be any drug, chemical or preparation which, according to standard works on medicine or materia medica, is liable to be destructive to adult human life in quantities of *sixty grains* or less.

No person shall sell at retail any poisons except as herein provided, without affixing to the bottle, box, vessel or package containing the same a label, printed or plainly written, containing the name of the article, the word “*poison*” and the name and place of business of the seller; nor shall he deliver poison to any person without satisfying himself that such poison is to be used for legitimate purposes.

It shall be the further duty of any one selling or dispensing poisons, which are known to be destructive to adult human life in quantities of five grains or less, before delivering them, to enter in a book kept for this purpose the name of the seller, the name and residence of the buyer, the name of the article, quantity sold or disposed of and the purpose for which it is said to be intended, which book of registry shall be preserved for at least two years, and shall at all times be open to the inspection of the coroner or courts of the county in which the same may be kept.

The provisions of this section shall not apply to the dispensing of physicians' prescriptions specifying poisonous articles, nor to the sale to agriculturists of such articles as are commonly used by them as insecticides. Any person failing to comply with the provisions of this section shall be deemed guilty of a misdemeanor, and upon conviction thereof shall be punished by a fine of not less than five nor more than fifty dollars for each and every offense.

Wood or methyl alcohol cannot be used in the compounding of pharmaceutical preparations.

The standards of law in this State do not permit the use of wood or methyl alcohol (this includes Columbian spirits, colonial spirits, kahol, etc.) in compounding and preparation of formulæ contained in the U. S. Pharmacopœia and National Formulary, and any one so using it will be subject to the penalties of the Act of May 25, 1897, and will be promptly dealt with by this Board according to law.

Penalty: Fine (\$100), imprisonment (90 days); either or both at discretion of court.

AN ACT.

Regulating the sale or prescription of cocaine, or of any patent or proprietary remedy containing cocaine, and prescribing penalties for the violation thereof.

Section 1. Be it enacted, etc., That no person shall sell, furnish or give away any cocaine, or any patent or proprietary remedy containing cocaine, except upon the prescription of a registered practicing physician, or of a dentist, or of a veterinarian; nor shall any such prescription be refilled; nor shall any physician, dentist or veterinarian prescribe cocaine, or any patent or proprietary remedy containing cocaine, for any person known to such physician, dentist or veterinarian to be an habitual user of cocaine: *Provided*, That the provisions of this Act shall not apply to persons engaged in the wholesale drug trade, regularly selling cocaine to persons engaged in the retail drug trade.

Section 2. Any person violating any of the provisions of this act shall be sentenced to pay a fine of not more than one hundred dollars and undergo an imprisonment of not more than six months, or both, or either at the discretion of the court.

Approved—The 22d day of April, A. D. 1903.

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